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HANDBOOK OF RADIOCHEMICAL ANALYTICAL METHODS

National Environmental Research Center

February 1975

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It should be noted that the procedures in the current compilation are intended for use in processing relatively large numbers of samples in the shortest possible time for environmental radiological surveillance and, therefore, in some cases represent a compromise between precise analytical determination and adequate determination for surveillance purposes.

For historical purposes, two methods for radiostrontium in milk are included since large numbers of samples were analyzed by these methods.

Appendix A provides instructions for preparing reagents listed for each method. It does not provide instructions for preparing solutions normally found in chemistry laboratories.

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HANDBOOK OF RADIOCHEMICAL ANALYTICAL METHODS

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Las Vegas, Nevada

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NATIONAL ENVIRONMENTAL RESEARCH CENTER
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
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PREFACE

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TABLE OF CONTENTS

Page

Rapid Ion Exchange Method for the Determination of Radiostrontium in Milk 1

Determination of Strontium-89 and Strontium-90 in Milk - Nitric Acid Procedure 7

Routine Ion Exchange Method for Strontium-89 and Strontium-90 in Milk 12

Preparation of Nonhomogeneous Samples for Analysis 20

Determination of Radiostrontium in Food and Bioenvironmental Samples 25

Determination of Calcium in Milk 30

Determination of Calcium in Food and Bone 32

Determination of Gross Alpha and Beta Activity in Water 34

Dissolution of Samples for Radium-226 Analysis 36

Determination of Radium-226 in Environmental Samples by Radon Emanation 39

The Determination of Radium-226 in Water Samples by Radon Emanation 42

The Analysis of Radium-226 in Soil, Ores and Mill Tailings . . . 44

The Apparatus and Method for Radon Transfer 48

Radon in Atmospheric Samples and Natural Gas 51

A Procedure for the Separation of Radiokrypton, Radioxenon, and Methane in Atmospheric Samples 55

Determination of Tritium in Water 63

Removal of Water from Blood, Milk, and Urine for Tritium Determination 66

Determination of Low Level Tritium in Water (Alkaline Electrolytic Enrichment) 68

The Collection and Determination of Tritium in the Atmosphere . 73

The Analysis of Food and Milk for Carbon-14 79

Page

Analysis of Uranium by Fluorometry 86

Radiochemical Determination of Thorium in Environmental Samples 95

Ion Exchange Separation of Plutonium 102

  Fresh Water 104

  Sea Water 106

  Urine 108

  Tissue Ash 110

  Bone Ash 112

  Preparation of Ion Exchange Column 117

  Construction and Assembly of Electrodeposition Cells 118

  Standardization and Computation 120

Determination of Polonium-210 and Lead-210 in Soil or Air Filters 125

APPENDIX A. Reagent Preparation 130

APPENDIX B. Decay Factors for Yttrium and Strontium 135

APPENDIX C. Decay Factors for Plutonium-236 140

FIGURES

Number		Page
1.	Ion Exchange Column	3
2.	Environmental Radiation Processor, Model B	23
3.	Fail Safe Circuit	24
4.	Strontium Adsorption Column and Filtering Apparatus	29
5.	Emanation Tube (Bubbler)	45
6.	Apparatus for Radon Transfer	50
7.	Apparatus for Radon in Air	52
8.	Flow Diagram for Separation of Methane, Krypton, and Xenon	62
9.	Distillation Apparatus	67
10.	Alkaline Electrolysis Cell	72
11.	Hydrogen in Air, Field Box	74
12.	Hydrogen in Air, Field Station	75
13.	Benzene Synthesis Apparatus	80
14.	Electroplating Cell	103

RAPID ION EXCHANGE METHOD FOR THE DETERMINATION OF RADIONSTRONTIUM IN MILK

PRINCIPLE OF THE METHOD

Milk with added carriers and disodium ethylenediaminetetraacetate (EDTA) is passed through a cation exchange resin. The alkali metals and most alkaline earths are adsorbed on the cation resin, and the complexed calcium passes through unadsorbed.

The alkaline earth metals are removed from the cation resin by elution with sodium chloride and precipitated as the carbonates. Barium is removed by chromate precipitation. Strontium-89 and strontium-90 are determined by counting twice, once after separation and again after yttrium-90 ingrowth, and strontium-89 decay. Chemical yield is determined gravimetrically.

Strontium-89 and -90 in sour milk may also be determined by this method using a batch process described on page 4 to adsorb the strontium.

REAGENTS

Ammonium acetate buffer solution: pH 5.2
Ammonium hydroxide: 6N, concentrated
Complexing solution
Dowex 50W-X8, 50-100 mesh
Ethyl alcohol: 95%
Ethylenediaminetetraacetate (EDTA), disodium: 3%
Nitric acid: 1N, concentrated, 90%
Sodium carbonate: 3N

Sodium chloride: 1.5N, 4N
Sodium chromate: 1N
Sodium hydroxide: 6N

APPARATUS

Centrifuge
Centrifuge bottles, 500-ml
Centrifuge tubes, 40-ml
Ion exchange columns
Low-background beta counter
Membrane filters, Millipore URWPO #2400
Membrane filter holders

PROCEDURE

A. For Fresh Milk

1. Add 300 ml EDTA complexing solution to one liter of milk filtered through cheese cloth and mix well. Pour the sample into funnel (Figure 1). Remove the screw cap from the bottom of cation column and allow the milk to pass through at gravity flow (approximately 100 ml/min).

2. Wash the resin with three 100-ml portions of hot distilled water, leaving enough water on the columns to keep them wet. Attach the stopcock assembly (Figure 1) to bottom of cation column. Add 800 ml hot (60° C) distilled water and allow to flow at a rate of 100 ml/min.

3. Add 800 ml of 3% EDTA (pH 5.2) at a flow of 20 ml/min to remove residual calcium, then add 200 ml distilled water.

4. Wash adsorbed EDTA from the column with 200 ml 1.5N sodium chloride at 10 ml/min. Place 500 ml of 4N sodium chloride in the funnel and let it flow through the column at a flow of 20 ml/min.

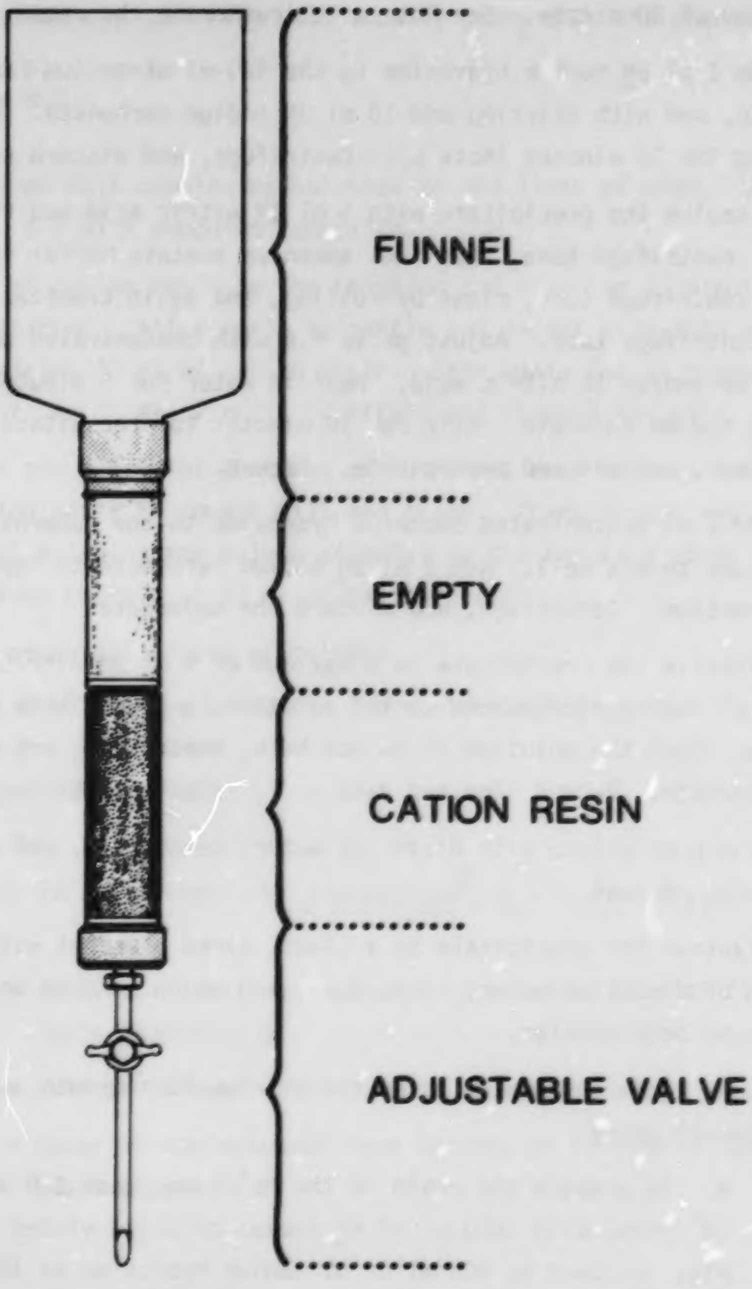
FUNNEL
EMPTY
CATION RESIN
ADJUSTABLE VALVE

Figure 1. Ion Exchange Column

5. Collect the first 400 ml of eluent in a 500-ml centrifuge bottle at a flow of 20 ml/min. See Note a to regenerate the resin.

6. Add 1 ml 6N sodium hydroxide to the 400-ml strontium-barium fraction, and with stirring add 10 ml 3N sodium carbonate. Continue stirring for 30 minutes (Note b). Centrifuge, and discard supernate.

7. Dissolve the precipitate with 5 ml 1N nitric acid and transfer to a 40-ml centrifuge tube. Add 5 ml ammonium acetate buffer (pH 5.25) to the centrifuge tube, rinse by rolling, and again transfer to a 40-ml centrifuge tube. Adjust pH to 4.6 with concentrated ammonium hydroxide and/or 1N nitric acid. Heat in water for 5 minutes and add 1 ml 1N sodium chromate. Stir for 10 minutes to precipitate barium. Centrifuge, and discard precipitate. Repeat.

8. Add 2 ml concentrated ammonium hydroxide to the supernate and swirl tube to mix well. Add 2 ml 3N sodium carbonate to reprecipitate the strontium. Centrifuge, and discard the supernate.

9. Dissolve the precipitate in a maximum of 6 ml 3N nitric acid. Add 30 ml fuming nitric acid to the solution to precipitate strontium nitrate. Cool the solution in an ice bath, centrifuge, and discard the supernate. Record time and data as T_1 (start of yttrium ingrowth).

10. Wash precipitate with distilled water, centrifuge, and discard supernate. Repeat.

11. Transfer the precipitate to a clean, tared planchet with a minimum of distilled water. Dry, cool, and weigh. Count on a low-background beta counter.

12. Count again seven days later for yttrium-90 ingrowth and strontium-89 decay.

Notes: a. To prepare the resin in the Na^+ form, wash 170 ml of resin (H^+ form) with 1000 ml of 4N sodium chloride eluted at 10 ml/min, followed by 400 ml of 5% sodium hydroxide at 10 ml/min, then 1000 ml of distilled water at 10 ml/min flow rate. Repack column and add glass fiber filter to top of column.

b. An occasional sample will not precipitate. Warming the solution with stirring will usually bring down the precipitate.

B. For Sour Milk

1. Add 300 ml EDTA complexing solution to one liter of milk. Stir, adjust pH to 5.2 with ammonium hydroxide.

2. Add 40 ml cation resin to the solution and stir for 15 minutes on a magnetic stirrer. Allow resin to settle and decant milk into another beaker containing 40 ml of cation resin. Stir again for 15 minutes on a magnetic stirrer. Allow resin to settle and discard the milk.

3. Combine the two 40-ml portions of resin and wash several times with distilled water to remove milk and cream. Transfer the resin into an 80-ml polyethylene column attached to the top of a 45-ml polyethylene column containing 30 ml of cation resin.

4. Attach reservoir to top of columns.

5. Proceed with the procedure for fresh milk beginning with step 3.

CALCULATIONS (Velton 1966)

$$\text{Strontium-90 (pCi/liter)} = \frac{DC - FA}{2.22ZYV[D(1 + EL) - F(1 + EI)]}$$

where D = decay of strontium-89 from collection to time of first count (Appendix B)

C = net cpm of total strontium on second count

F = decay of strontium-89 from collection to time of second count (Appendix B)

Velton, R. J., Resolution of Strontium-89 and Strontium-90 in Environmental Media by an Instrumental Technique. Nucl Instr Methods 42:169 (1966)

A = net cpm of total strontium on first count

2.22 = dpm/pCi

Z = fractional counting efficiency for strontium-90 including self-absorption correction

Y = fractional chemical yield

V = sample volume in liters

E = ratio of yttrium-90 counting efficiency to strontium-90 counting efficiency including self-absorption corrections

L = yttrium-90 ingrowth from time of separation to time of second count

I = yttrium-90 ingrowth from time of separation to time of first count

$$\text{Strontium-89 (pCi/liter)} = \frac{A - N(1 + IE)}{2.22DYSV}$$

where A = net cpm total strontium on first count

N = net cpm strontium-90; this is first factor in the equation for strontium-90 in pCi/liter

I = yttrium-90 ingrowth from separation to time of first count

E = ratio of yttrium-90 counting efficiency including self-absorption corrections

2.22 = dpm/pCi

D = decay of strontium-89 from collection to time of first count

Y = fractional chemical yield of strontium

S = fractional counting efficiency for strontium-89

V = sample volume in liters

DETERMINATION OF STRONTIUM-89 AND STRONTIUM-90 IN MILK
NITRIC ACID PROCEDURE
(This procedure was used from 1960 to 1966.)

PRINCIPLE OF THE METHOD

After the addition of a strontium carrier, the milk proteins are precipitated with trichloroacetic acid. Following filtration, excess oxalic acid is added to the filtrate and the alkaline earths are precipitated as the oxalates at pH 3.0. The oxalates are then converted to the nitrates. Calcium and strontium are separated by differences in solubility. The strontium is scavanged with barium, iron, and rare earth carriers. After a final nitric acid extraction of yttrium-90, the strontium precipitate is stored for a minimum of one week to allow for yttrium ingrowth. After this period, the strontium is reprecipitated with 70% nitric acid, and yttrium is recovered in the supernate. Both fractions are mounted on a planchet and counted for beta activity.

The strontium-89 activity is the calculated difference between total strontium activity and the strontium-90 (as yttrium-90 activity).

REAGENTS

Acetic acid: 1.5N
Ammonium acetate: 3N
Ammonium acetate buffer: pH 5
Ammonium hydroxide: 1N, 6N, concentrated
Barium carrier: 5 mg Ba^{2+}/ml
Bromocresol green indicator
Hydrochloric acid: 0.5N, concentrated
Hydrogen peroxide: 30%

Mixed rare earth carrier

Nitric acid: 0.5N, 1N, 3N, concentrated, 90%

Oxalic acid: saturated at room temperature

Sodium chromate: 1N

Sodium carbonate: 3N

Strontium carrier: 8 mg Sr^{2+}/ml

Trichloroacetic acid: 50%

APPARATUS

Buchner funnel

Filter sticks, medium porosity

Low-background beta counter

Stainless steel planchets, 5.08-cm (2-inch) diameter

PROCEDURE

1. Place a 1000-ml aliquot of sample into a 2000-ml beaker. Add strontium carrier (80.0 mg) and stir solution thoroughly.

2. Add 300 ml of 50% trichloroacetic acid (TCA) to the solution with stirring. Filter the solution through Whatman #2 filter paper into a Buchner funnel and collect filtrate in a 3000-ml flask. Wash precipitate with three portions of distilled water.

3. Transfer filtrate into a 2000-ml beaker and rinse the flask with distilled water. Add 125 ml of saturated oxalic acid to the solution and thoroughly mix. Adjust pH to 3.0 with concentrated ammonium hydroxide, using a pH meter. Allow 5 to 6 hours for precipitate to settle.

4. Aspirate the supernate through a medium porosity filter stick. Wash the beaker and precipitate with three portions of distilled water.

5. Transfer precipitate to a 250-ml beaker with concentrated nitric acid, placing the filter stick in the beaker. Heat the beaker on a hot

plate until precipitate separates from the filter stick. Rinse the filter stick inside and out with concentrated nitric acid and remove.

6. Evaporate the solution to near dryness. Add 50 ml of concentrated nitric acid and evaporate to near dryness. Repeat until the residue is colorless.

7. Transfer the residue to a 40-ml centrifuge tube with a minimum of concentrated nitric acid, and then cool the solution overnight in refrigerator. Centrifuge at 1500-1800 rpm for ten minutes. Discard the supernate.

8. Dissolve the precipitate in 5 ml of 3N nitric acid and add 10 ml of fuming nitric acid. Centrifuge the mixture, and discard the supernate.

9. Dissolve precipitate in 5 ml water. Add three drops of bromocresol green indicator to the solution. Add 6N ammonium hydroxide until the color changes from yellow to blue. Use 0.5N nitric acid to back titrate until the solution barely turns yellow. Add 5 ml of ammonium acetate buffer solution and 1.0 ml of barium carrier. Heat solution in a water bath and add 1.0 ml of 0.25N sodium chromate. Heat solution until a definite barium chromate precipitate is noticed. Cool solution and filter through a Whatman #42 filter paper into a 250-ml beaker. Wash precipitate with distilled water.

10. Add 5 drops of mixed rare earth carrier, 2 drops hydrochloric acid, and 5 drops of 30% hydrogen peroxide to the filtrate. Warm the solution and add concentrated ammonium hydroxide until a precipitate forms. Filter the solution through a Whatman #42 filter paper and wash with distilled water.

11. Allow the filtrate to evaporate to approximately 10 ml and transfer to a 40-ml centrifuge tube with concentrated ammonium hydroxide. Add 5 ml concentrated ammonium hydroxide and 2 ml 3N sodium carbonate. Mix the solution, cool, and centrifuge. Discard the supernate.

12. Dissolve precipitate in a maximum of 6 ml of 3N nitric acid. Add 30 ml of fuming nitric acid to the solution. Cool the solution and centrifuge. Discard the supernate. Record time and date as T_1 (start of yttrium ingrowth). (Total radiostrontium may be determined at this point.) Store the precipitate for a minimum of one week.

13. After a suitable ingrowth period, dissolve the strontium nitrate precipitate with 5 ml water.

14. Add 30 ml of fuming nitric acid and cool the solution in an ice bath. Record time and date as T_2 (completion of ingrowth).

15. Centrifuge the solution and decant the supernate into a 250-ml beaker

16. Dissolve the residue in 6 ml of distilled water and repeat steps 15 and 16, combining the supernates.

17. Evaporate supernate to a small volume and transfer with 3N nitric acid to a stainless steel planchet. Evaporate the solution to dryness and submit for beta counting of yttrium-90.

18. Transfer the precipitate with distilled water into a tared planchet and evaporate to dryness. Determine the weight of the residue for self-absorption correction and submit for beta counting of total strontium-89 and -90.

CALCULATIONS

$$\text{Strontium-89 + -90 (pCi/liter)} = \frac{C}{2.22EYV}$$

$$\text{Strontium-90 (pCi/liter)} = \frac{N}{2.22AYIDV}$$

$$\text{Strontium-89 (pCi/liter)} = \frac{(\text{pCi } {}^{89}\text{Sr} + {}^{90}\text{Sr}) - \text{pCi } {}^{90}\text{Sr}}{B}$$

where C = cpm total radiostrontium counted

2.22 = dpm/pCi

E = counting efficiency for strontium-90 including self-absorption

Y = chemical yield for strontium

V = volume of sample taken in liters

N = cpm yttrium-90

A = counting efficiency for yttrium-90

I = ingrowth of yttrium-90 from T_1 to T_2

D = decay of yttrium-90 from T_2 to time of count

B = decay of strontium-89 from time of collection to time of count

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Murthy, G. K., et al. A Method for the Elimination of Ashing in Strontium-90 Determination of Milk. Dairy Science 43:151-4 (1960)

ROUTINE ION EXCHANGE METHOD FOR STRONTIUM-89 AND STRONTIUM-90 IN MILK

(This procedure was used from 1966 to 1968.)

PRINCIPLE OF THE METHOD

Milk with added citrate solution containing yttrium, strontium, and barium carriers is passed successively through cation and anion exchange resin columns. Strontium, barium, and calcium are adsorbed on the cation exchange resin, and the yttrium carrier, with the yttrium-90 daughter of strontium-90, is retained on the anion exchange resin. The yttrium is eluted from the anion resin with hydrochloric acid and precipitated as the oxalate. Lanthanum-140 may be a contaminant. To remove the lanthanum contaminant, yttrium oxalate is dissolved in concentrated nitric acid and yttrium extracted from the solution into an equal volume of pre-equilibrated tributyl phosphate. The lanthanum-140 remains in the concentrated nitric acid to be discarded. Yttrium is re-extracted from the organic phase with dilute nitric acid and precipitated as the oxalate. The precipitate is weighed to determine recovery of yttrium carrier, then counted.

Calcium, strontium, and barium are eluted from the cation exchange resin with sodium chloride solution. The alkaline earth metals are precipitated as carbonates and nitrates. (The latter precipitation affords a separation of strontium from calcium.) Barium is removed from the strontium by chromate precipitation and strontium nitrate is counted for total radionstrontium. The yield is determined by flame spectrophotometry.

REAGENTS

Ammonium acetate buffer solution
Ammonium hydroxide: concentrated
Barium carrier: 2.0 mg Ba^{2+}/ml
Citrate solution
Dowex 1-X8, 20-50 mesh
Dowex 50W-X8, 50-100 mesh
Hydrochloric acid: 2N, 6N
Nitric acid: 0.1N, 6N, 14N concentrated, 90%
Oxalic acid: 1N
Sodium carbonate: 3N
Sodium chloride: 4N
Sodium chromate: 3N
Strontium carrier: 2.0 mg Sr^{2+}/ml
Tributyl phosphate (TBP)
Yttrium carrier: 1.0 mg Y^{3+}

APPARATUS

Ion exchange system (Kontes K-42753 or equivalent)
Stainless steel planchets, 5.08-cm (2-inch) diameter

PROCEDURE

A. Preliminary Separation

1. Place one liter of milk (Note a) in the reservoir. Add 10 ml each of yttrium, strontium, and barium carriers to 10 ml citrate solution and stir the mixture to dissolve barium citrate. Quantitatively transfer the carrier-citrate solution with a minimum amount of distilled water and shake it vigorously. Place the reservoir above the anion column.

2. Open the stopcocks on the reservoir, the anion column, and the cation column in that order. Control the flow rate to 10 ml/min with the anion column stopcock (Note b). Allow the milk to flow only until enough milk is left in the columns to cover the resins. Discard effluent milk. Record the midpoint of the elution time as the start of the yttrium-90 decay.

3. Replace the milk reservoir with a separatory funnel containing 300 ml warm (40° C) distilled water and wash the columns with the water at a flow rate of 10 ml/min to displace the milk. Again, stop the flow when the water just covers the resin. Discard effluent water.

4. Separate the ion exchange columns. (The top cation exchange column is used for total radiostrontium determination in steps 20 to 29. The lower anion exchange column is used for the strontium-90 determination.)

B. Strontium-90 Determination

5. Attach a separatory funnel containing 100 ml 2N hydrochloric acid to the top of the anion exchange column and begin elution at 2 ml/min. Continue flow until the pH of the effluent drops to 2, as determined with pH paper on drops of effluent as they fall off the bottom of the column. Discard the effluent. Collect the next 10 ml of effluent. Then stop flow. Remove the separatory funnel and stir the resin thoroughly with a stirring rod. Wash the stirring rod with 2N hydrochloric acid and add the washings to the resin. Attach the separatory funnel and continue elution until a total of 35 ml of eluate has been collected. Process the eluate containing the yttrium-90 as described in steps 7 and 19 below.

6. Pass the remaining 2N hydrochloric acid through the anion exchange column at 10 ml/min to recharge the column. Wash the resin with 100 ml water at 2 ml/min (Note c). The resin is then ready for reuse.

7. To precipitate Y^{3+} from the eluate in step 5, add 5 ml 1N oxalic acid and adjust the pH of the solution to 1.5 with concentration ammonium hydroxide using a pH meter. Stir the solution while heating to near boiling. Cool in an ice bath for approximately 20 minutes, and centrifuge. Discard the supernate.

8. If fresh fission products are present in the sample, follow steps 9 through 19. If fresh fission products are not present, the lanthanum extraction procedure (steps 9 through 14) may be omitted. If omitted, perform step 8a. Then continue beginning with step 15.

8a. Wash the precipitate with 10 ml hot distilled water and centrifuge. Discard the supernate. Then dissolve the precipitate in 1 ml 6N hydrochloric acid and 15 ml hot distilled water. If insoluble material remains, centrifuge the solution and discard the solid residue. Analyze the supernate as described beginning with step 15.

9. Dissolve the precipitate in 14N nitric acid and transfer the solution to a 60-ml separatory funnel. Wash the centrifuge tube with 10 ml pre-equilibrated tributyl phosphate (TBP), and add the washing to the separatory funnel.

10. Extract the Y^{3+} into the TBP by vigorous shaking for two to three minutes. After phase separation, discard the lower, aqueous phase.

11. Wash the TBP with 15 ml 14N nitric acid by shaking two to three minutes. Discard the lower, aqueous phase.

12. Repeat step 11.

13. Strip the Y^{3+} from the TBP by vigorous shaking with 15 ml distilled water for two to three minutes. Drain the lower, aqueous phase into a 40-ml centrifuge tube.

14. Repeat step 13 using 10 ml 0.1N nitric acid instead of water, and add the lower, aqueous phase to that obtained in step 13.

15. Precipitate the Y^{3+} as the oxalate by adding 5 ml 1N oxalic acid and ajusting the pH to 1.5. Stir the solution and cool in an ice bath

for approximately 20 minutes. After centrifugation, discard the supernate.

16. Wash the yttrium oxalate precipitate twice with water and transfer onto a tared stainless steel planchet using a minimum amount of water.

17. Dry the planchet on a hot plate taking care that the precipitate is not seared.

18. After cooling, reweigh the planchet to determine yttrium recovery.

19. Count the planchet in a low-background beta counter.

C. Total Radiostrontium Determination

20. Elute the alkali metals and alkaline earths from the top cation column referred to in step 4 with 1 liter 4N sodium chloride flowing at a rate of 10 ml/min. Collect the eluate to a total volume of 1 liter.

21. Wash the resin with 500 ml distilled water and discard the eluate. The resin is ready for reuse.

22. Heat the sodium chloride solution from step 20 to 85°-90° C on a hot plate and add 100 ml 3N sodium carbonate with stirring. Remove the solution from the hot plate and allow to cool to room temperature. Decant the bulk of the supernate and transfer the precipitate of alkaline earth carbonates with water to a 250-ml centrifuge bottle. Centrifuge the solution and discard the supernate. Wash the precipitate twice with water.

23. Dissolve the carbonate precipitate in a minimum amount of 6N nitric acid, heating in a hot water bath if necessary to aid in the dissolution. Filter the solution into a 40-ml graduated centrifuge tube. Discard the filter paper and contents.

24. To the filtrate add a sufficient volume of fuming nitric acid (as shown in the table) to obtain a 70% nitric acid concentration. Stir the solution, cool in an ice bath, and centrifuge. Discard the supernate.

NITRIC ACID PROPORTIONS FOR STRONTIUM AND BARIUM PRECIPITATIONS

To Volume of 6N Nitric Acid (ml)	Add Amount of 90% Nitric Acid (ml)	To Obtain Final Conc. of (%)
8	15	69.8
9	17	69.9
10	19	70.0
11	21	[illegible]0.1
12	22	69.5
13	24	69.6
14	26	69.7
15	28	69.8

If the volume of 6N nitric acid exceeds 15 ml, transfer to a 250-ml centrifuge bottle with 6N nitric acid and add a bulk of 90% nitric acid (150-200 ml). Cool, centrifuge, and discard supernate. Wash precipitate with concentrated nitric acid, centrifuge, and discard supernate.

25. Dissolve the strontium-barium nitrate precipitate in 5 ml water and add 5 ml ammonium acetate buffer. The pH should be 5 as determined with pH paper.

26. Heat the solution in a water bath and add 1 ml 3N sodium chromate with stirring. Centrifuge the solution. Decant the supernate into a clean 40-ml centrifuge tube and discard the barium chromate precipitate.

27. Add 30 ml fuming nitric acid to the supernate from step 26. Cool the solution, centrifuge, and decant the supernate. Record the time of decantation as start of yttrium-90 ingrowth.

28. Dissolve the precipitate in a minimum amount of water and transfer quantitatively onto a stainless steel planchet. Evaporate the solution to dryness on a hot plate, cool, and count in a low-background beta counter.

29. Dissolve the residue on the planchet in water and transfer quantitatively to a 250-ml volumetric flask. Dilute the solution to the mark,

shake well, and pipet 20 ml into a 100-ml volumetric flask. Dilute to the mark with water and submit for strontium yield determination

Notes: a. The milk must be reasonably homogeneous, preserved with formaldehyde, and refrigerated (approximately 0° C) for two weeks to allow the yttrium-90 to come to equilibrium with the strontium-90.

b. If the stoppers in the cation and the anion columns are airtight, flow can be adjusted using only the anion column stopcock.

c. Trapped milk particles can be removed from the column by backwashing with water or in a beaker by slurrying the resin with water.

CALCULATIONS

$$\text{Strontium-90 (pCi/liter)} = \frac{C - B}{2.22EYVDI}$$

where C = cpm obtained by counting yttrium oxalate

B = cpm background

2.22 = dpm/pCi

E = fractional counting efficiency for yttrium-90

Y = fractional yield of yttrium carrier

V = volume of sample in liters

D = correction factor for yttrium-90 decay ($e^{-\lambda t}$) where t is the time from the midpoint of the elution time to the time of counting, and λ is the decay constant for yttrium-90.

I = correction factor for degree of yttrium-90 ingrowth ($1-e^{-\lambda t}$) where t is the time from the collection of the milk sample to the time of passage through the column.

$$\text{Strontium-89 (pCi/liter)} = \frac{C - B}{2.22EDYV} - 2.22S(F - GI)$$

where C = cpm obtained by counting strontium nitrate

B = cpm background

2.22 = dpm/pCi

S = pCi/liter strontium-90 as calculated above

F = fractional counting efficiency for strontium-90 including the self-absorption factor

G = fractional counting efficiency for strontium-90

I = correction factor for yttrium-90 ingrowth $(1-e^{-\lambda t})$ where t is the time from the last decantation of nitric acid from the strontium nitrate precipitate to the time of counting

E = fractional counting efficiency for strontium-89

D = correction factor for strontium-89 decay $(e^{-\lambda t})$ where t is the time from sample collection to time of counting, and λ is the decay constant for strontium-89.

Y = fractional yield of strontium carrier

V = volume of milk sample in liters

PREPARATION OF NONHOMOGENEOUS SAMPLES FOR ANALYSIS

PRINCIPLE OF THE METHOD

This procedure describes methods for the grinding, blending, and ashing of food, bone, tissue, vegetation, and rumen samples. The food is ground and blended in an Environmental Residue Processing Apparatus, an apparatus built at NERC-LV to combine grinding and blending of total diet samples. The other biological samples are cleaned and ashed to remove all traces of organics.

REAGENTS

Formalin

APPARATUS

Balance, 10 kg
Environmental Residue Processing Apparatus (Figures 2 and 3)
Marinelli beaker, 3.5-liter
Muffle furnace
Porcelain casserole, 1800-ml
Wiley Mill

PROCEDURE

A. For Institutional Surveillance Diet Network Samples

1. Obtain weights of all containers plus samples.
2. Add the liquid fractions to the blender. (Figure 2)

3. Start blender/grinder and add solid portions, checking and removing inedible items (record these items).

4. Allow sample to circulate for 10 minutes. Add 10 ml formalin to total sample.

5. Weigh the empty containers to obtain net weights of liquids and solid portion.

6. Stop blender and record volume of sample.

7. Transfer 3.5 liters of blended sample to a Marinelli beaker, and submit for gamma spectroscopy analysis.

8. Transfer the remaining blended sample to tared 1800-ml casseroles and reweigh. Proceed to step C-1.

9. Clean the blender/grinder with soap and water. (Notes a, b, and c.)

B. For Bone, Tissue, Vegetation, and Rumen Samples

1. Remove all visible foreign matter from samples. Divide the larger pieces by sawing. Using compaction if necessary, transfer all of the sample to tared 1800-ml casseroles and weigh. Proceed to step C-1.

C. Ashing

1. Place the casseroles (from step A-8 and B-1) in muffle furnace and dry at 150° C overnight or longer.

2. Increase the temperature (common sense is best indicator) gradually until 600° C is reached. Hold at this temperature until the ash is powdery and light grey or tan in color. Prolonged ignition or overheating of high phosphate sample (eggs, pork, beef) should be avoided, as a phosphate "glass" which is difficult to dissolve tends to form. An occasional grinding with a pestle will speed up the ashing.

3. After ashing is complete, turn off furnace and allow to cool.

4. Weigh the food ash and grind with a mortar and pestle. Grind the bone ash in the Wiley Mill.

Notes: a. Do not allow pump to operate without water or sample in the reservoir. The rubber impeller is subject to severe wear when running dry.

b. A small quantity of water will remain in the lower parts of the apparatus. To remove before operation, remove drain plug and drain into a beaker.

c. The fail-safe circuit (Figure 3) is designed to turn off the pump in case the thermal overload breaker on the disposal unit trips. When this happens, turn off switch, check the disposal blade for jamming, turn on switch, and push the overload button located on the disposal unit. This will start the apparatus again.

CALCULATIONS

To obtain total ash weight of the food sample:

$$\text{ash (g)} = \frac{AB}{B - 3.5}$$

where A = weight of combined ash, in grams

B = volume of total blended sample, in liters

3.5 = volume of Marinelli beaker, in liters

To obtain % ash weight for food:

$$\text{ash (\%w)} = \frac{C}{10D}$$

where C = total ash weight, in grams

D = total sample weight, in kilograms

To obtain % ash weight for bone, tissue, etc.:

$$\text{ash }(\%w) = \frac{100C}{E}$$

where C = total ash weight, in grams

E = total sample weight, in grams

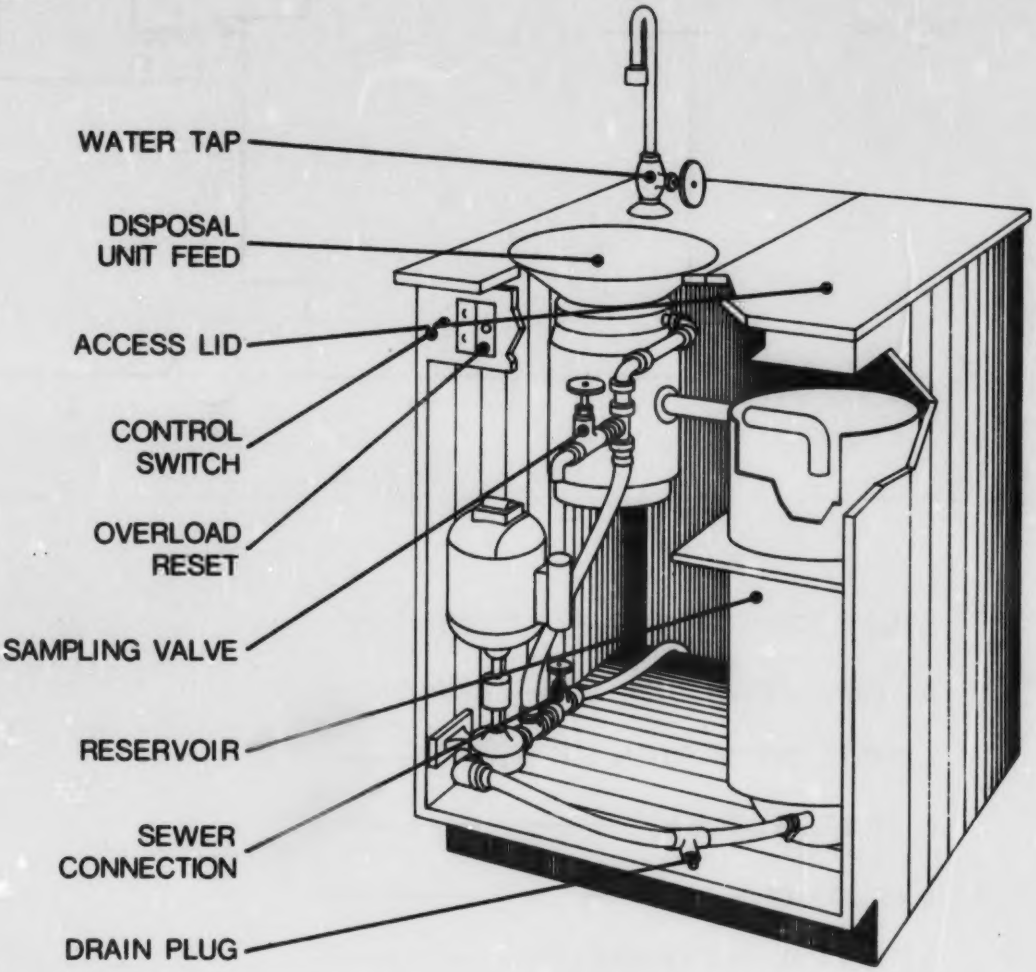
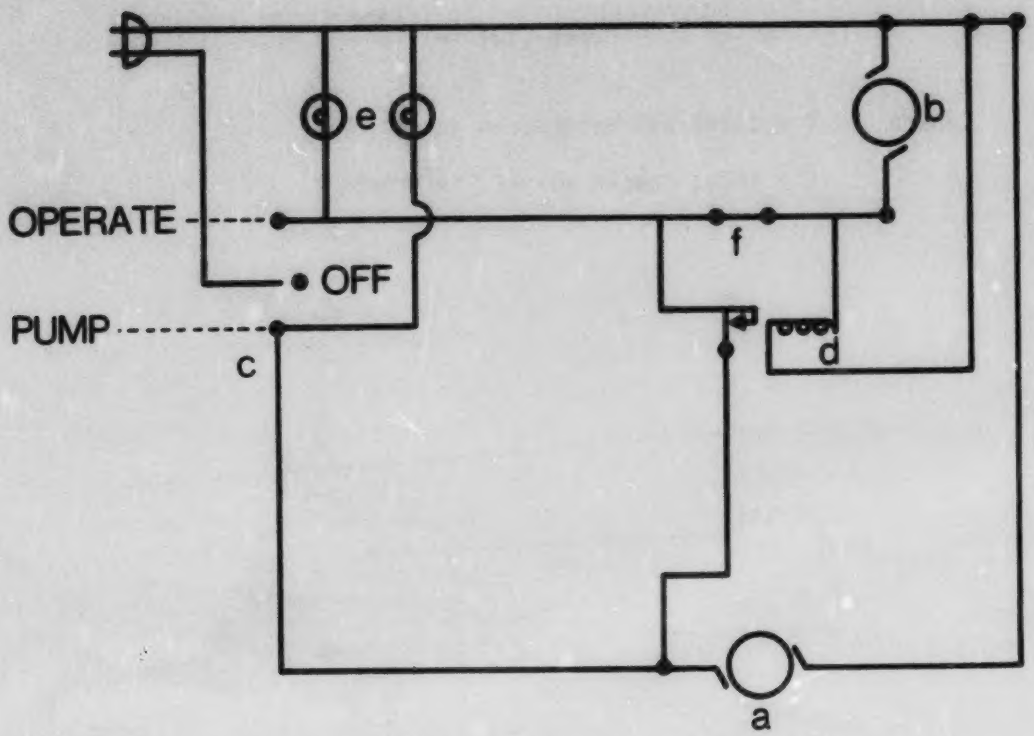

WATER TAP
DISPOSAL UNIT FEED
ACCESS LID
CONTROL SWITCH
OVERLOAD RESET
SAMPLING VALVE
RESERVOIR
SEWER CONNECTION
DRAIN PLUG

Figure 2. Environmental Radiation Processor, Model B


e
b
OPERATE
f
OFF
PUMP
c
d
a

a. 1/3 hp CAPACITOR START MOTOR ________

b. YOUNGSTOWN FOOD WASTE DISPOSAL ___

c. S.P.D.T. OFF POSITION BAT SWITCH ________

d. S.P.S.T. RELAY ________

e. PILOT LIGHTS ________

f. THERMAL SWITCH OFF ________

Fiqure 3. Fail Safe Circuit

DETERMINATION OF RADIOSTRONTIUM IN FOOD AND BIOENVIRONMENTAL SAMPLES

PRINCIPLE OF THE METHOD

This method describes a procedure for the determination of strontium-89 and -90 in various bioenvironmental samples. The ash is fused as a carbonate, the strontium-calcium carbonates are dissolved in hydrochloric acid, complexed with disodium ethylenediaminetetraacetate (EDTA), passed through an ion exchange column where the strontium is adsorbed, and the complexed calcium passes through. The strontium is eluted, precipitated as a carbonate, and mounted on a planchet for beta counting. Chemical yield is determined gravimetrically.

REAGENTS

Ammonium hydroxide: concentrated
Barium carrier
Calcium carrier
Ethylenediaminetetraacetate (EDTA), disodium: 6%, 2%
Hydrochloric acid: 6N, 1.5N
Sodium acetate buffer solution
Sodium carbonate, anhydrous: 3N
Sodium chloride
Sodium hydroxide pellets
Strontium carrier

APPARATUS

Crucible with cover, nickel, 250-ml

Bath, cooling

pH meter

Funnel, separatory, graduated, 1000-ml

Column, 2.5-cm I.D. (Figure 4), 40-ml cation resin Dowex 50W-X8, 50-100 mesh

Filter paper, Millipore #URWPO 2400

PROCEDURE

A. For Food, Vegetation, or Tissue

1. Weigh amount of sample shown in table and place in a 250-ml nickel crucible. Add carriers as indicated, 50 g sodium hydroxide pellets, and 5 g anhydrous sodium carbonate. Mix and cover.

VARIOUS SAMPLE TYPES, SAMPLE SIZE, AND CARRIERS

Sample Type	Sample Size (g)	Strontium Carrier (ml)	Calcium Carrier (ml)	Barium Carrier (ml)
Food	10	2	--	5
Bone	2	2	--	5
Vegetable	2 or 5	2	1	5
Tissue	2	2	1	5

2. Carefully heat over a burner until melt dissolves. Then raise temperature and fuse for 60 minutes or until melt is red hot.

3. Transfer crucible with cover to cold water bath to crack mixture. Cool.

4. Add 200 ml hot distilled water, and boil to disintegrate the fused mixture.

5. Cool, and transfer to 250-ml centrifuge tube. Centrifuge, and discard supernatant solution. Repeat twice with 200-ml portions of hot distilled water.

6. Add 20 ml 6N hydrochloric acid and with gentle heat dissolve the residue. Add 100 ml distilled water. If insoluble residue (silica) is present, filter, wash residue twice with 100-ml portions of distilled water, and add to filtered solution. Discard residue.

7. Add filtrate to 500 ml 6% EDTA solution and adjust to pH 3.8 with concentrated ammonium hydroxide. Stir vigorously for 75 minutes to precipitate the magnesium salt of EDTA.

8. Filter, and collect the filtrate. Adjust to pH 4.6 with ammonium hydroxide. Add 20 ml buffer solution. Re-adjust pH to 4.6.

9. Quantitatively transfer to the 1000-ml graduated cylinder and dilute to 1000 ml with distilled water.

10. Adjust solution flow through resin column to 10 ml/min. Stop flow when just enough solution remains to cover resin. Discard effluent.

11. Adjust 600 ml 2% EDTA to pH 5.1 with ammonium hydroxide, place in reservoir, and let flow at 20 ml/min. Record time at end of elution as T_1 (beginning of yttrium-90 ingrowth). Wash column with 200 ml distilled water at a flow of 20 ml/min. Discard washings.

12. Place 460 ml 1.5N hydrochloric acid in reservoir, and elute at a flow rate of 8 ml/min. Discard first 60 ml of effluent. Collect the next 400 ml in a 800-ml beaker. This contains the strontium fraction.

13. Regenerate resin with 600 ml 4N sodium chloride followed by 1000 ml distilled water, both at a flow rate of 10 ml/min.

14. Add 200 ml concentrated ammonium hydroxide to the strontium fraction with stirring. Slowly add 10 ml 3N sodium carbonate, and stir 30 minutes.

15. Filter (Figure 4) using Millipore filter paper #URWPO 2400. Rinse the beaker with distilled water. Police sides and bottom of beaker. Wash walls of beaker and filter with ethyl alcohol.

16. Remove funnel and wash any precipitate on the bottom of the funnel directly into weighed planchet with minimum amount of water. Wash the precipitate from the filter paper directly into the weighed planchet.

17. Evaporate to dryness. Cool and weigh.

18. Let sample set overnight for radon daughter decay and count in a low-background beta counter.

19. Count again seven days later for yttrium-90 ingrowth.

B. For Water

Add 33.3 g EDTA, 2 ml strontium carrier, and 1 ml each barium and calcium carriers to 1000 ml of water sample. Adjust pH to 4.6 with ammonium hydroxide and proceed as in step 8 of Procedure A.

C. For Seawater

1. Add 2 ml strontium carrier, and 1 ml each barium and calcium carriers to 1000 ml of water sample. Stir and heat to boiling.

2. Adjust pH to 10.0 with 6N sodium hydroxide. Add 30 ml 3N sodium carbonate. Stir and continue heating until precipitate forms. Cool overnight and decant the supernate.

3. Dissolve residue with 200 ml 6N hydrochloric acid. Adjust volume to 1 liter with distilled water, and filter. Add 33.3 g EDTA with stirring and adjust pH to 3.8. Proceed as in step 7 of Procedure A.

D. For Bone

Weigh 2.0 grams of ash in a 1000-ml beaker. Moisten with water, and add 20 ml 6N hydrochloric acid. When ash is dissolved, add 100 ml water and proceed as in step 7 of Procedure A.

CALCULATIONS

Refer to calculations for the Rapid Ion Exchange Method for the Determination of Radiostrontium in Milk, page 5, making appropriate changes in V for aliquot size.

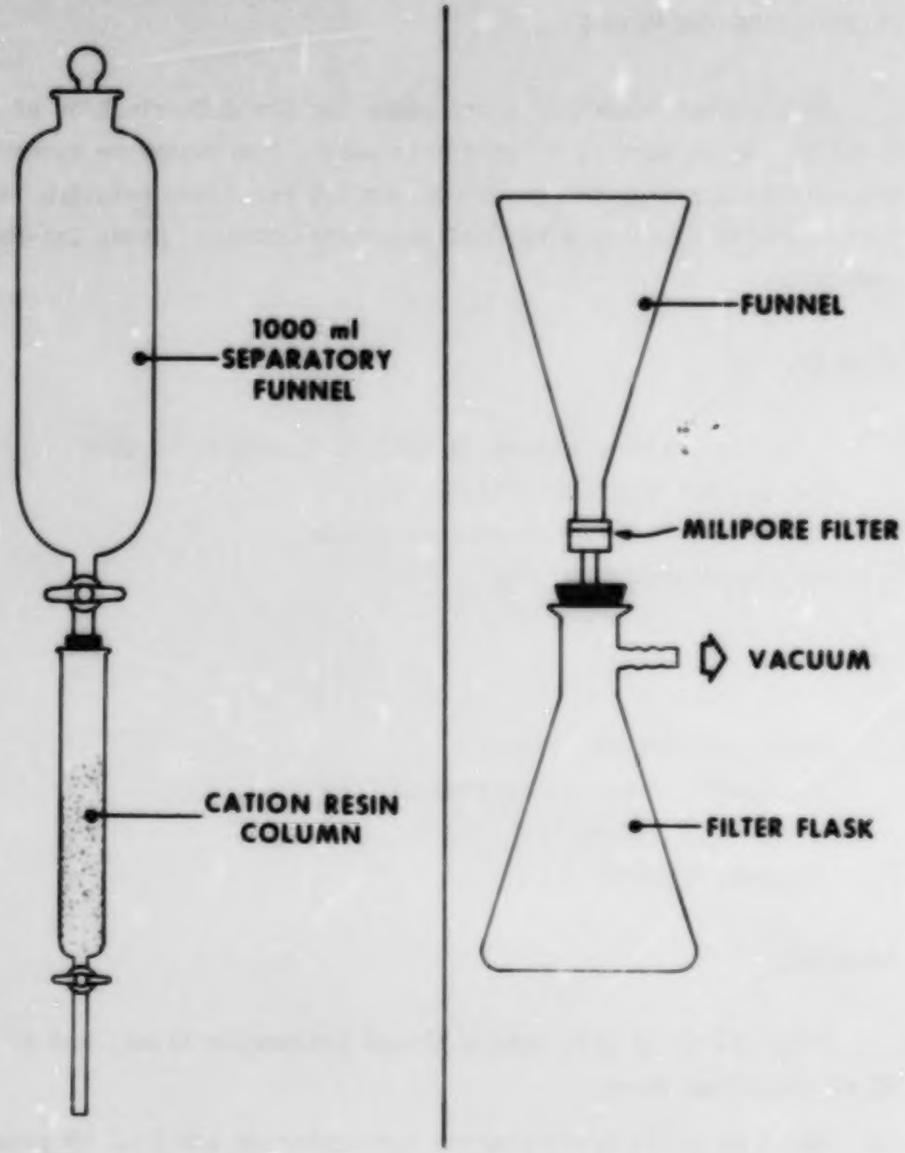

1000 ml
SEPARATORY
FUNNEL
CATION RESIN
COLUMN
FUNNEL
MILIPORE FILTER
VACUUM
FILTER FLASK

Figure 4. Strontium Adsorption Column and Filtering Apparatus

DETERMINATION OF CALCIUM IN MILK

PRINCIPLE OF THE METHOD

This method describes a procedure for the determination of calcium in milk. An aliquot is diluted with water, hydroxylamine hydrochloride and potassium hydroxide are added, and the resulting solution is titrated with disodium ethylenediaminetetraacetate, using Cal-Red indicator.

REAGENTS

Ethylenediaminetetraacetate (EDTA), disodium: 0.004*N*
Hydroxylamine hydrochloride: 5%
Indicator, "Cal-Red" Indicator Dilute
Potassium hydroxide: 5*N*

APPARATUS

Flask, Erlenmeyer, 125-ml
Microburet, 5-ml, calibrated in 0.01
Pipet, 5-ml, 10-ml
Stirrer, magnetic

PROCEDURE

1. Pipet 10 ml of milk into a 125-ml Erlenmeyer flask, and dilute with 50 ml distilled water.

2. Add 5 ml of 5% hydroxylamine hydrochloride and 5 ml 5*N* potassium hydroxide.

3. Add Teflon stir bar and mix well, let stand no less than three minutes and no more than five minutes.

4. Add approximately 0.1 g of Cal-Red indicator, and titrate immediately with 0.004N EDTA. At the end point the solution will change from a lavender color to baby blue. If end-point fades, make new potassium hydroxide.

CALCULATIONS

$$\text{Calcium (g/liter)} = \frac{ABC}{D}$$

where A = equivalent weight for calcium

B = volume of EDTA (ml)

C = normality of EDTA (eq/liter)

D = sample volume (ml)

DETERMINATION OF CALCIUM IN FOOD AND BONE

PRINCIPLE OF THE METHOD

The ashed sample is weighed and dissolved with 6N hydrochloric acid. Following filtration, excess oxalic acid is added and the alkaline earths are precipitated as the oxalates at pH 3. The calcium is precipitated as the oxalate so as to remove the interfering ions of sodium, potassium, and phosphate which depress the calcium emission. The oxalates are converted to nitrates, and the calcium determined by EDTA titration.

REAGENTS

Ammonium hydroxide: 6N
Ammonium oxalate: 0.5% solution
Hydrochloric acid: 6N
Nitric acid: 3N
Oxalic acid: crystal

PROCEDURE

1. Weigh 1.0 g of food ash in 250-ml beaker.

2. Dissolve the ash with 3N hydrochloric acid and filter through Whatman No. 2 paper. Discard filter paper.

3. Immediately add 10 ml of saturated oxalic acid to the sample. Mix thoroughly.

4. Adjust pH of the cool solution to 3.0 with 6N ammonium hydroxide using pH meter. (Standardize with pH 4 buffer.) Let solution stand overnight.

5. Filter the sample through Whatman No. 42 paper. Wash precipitate several times with water.

6. After filters are nearly dry, place them in a medium-sized (50-mm) crucible and ash for several hours at 575° F. Wet with concentrated nitric acid and put in hot muffle furnace for 15 seconds. Cool.

7. Dissolve ash in 2-3 ml 3N nitric acid. Transfer to a 100-ml volumetric flask with several distilled water washings and bring the flask up to volume with distilled water.

8. Shake flask thoroughly, then pipet a 10-ml aliquot into a 125-ml Erlenmeyer flask for EDTA titration. (If little calcium is present a larger aliquot may be taken.) Follow procedure for determination of calcium in milk (page 30), starting at step 1 and dilute with 50 ml demineralized water.

CALCULATION

$$\text{Calcium (mg/g ash)} = \frac{1000A}{BC}$$

where A = ml EDTA used to titrate 10 ml standard solution (1 g/l)

B = ml EDTA used to titrate sample

C = ml sample aliquot taken in step 8 (usually 10 ml)

DETERMINATION OF GROSS ALPHA AND BETA ACTIVITY IN WATER
(TOTAL, OR SUSPENDED AND DISSOLVED SOLIDS)

PRINCIPLE OF THE METHOD

This method describes procedures for the determination of gross alpha and beta activity in natural waters. This activity is not indicative of any specific nuclide; however, it does provide an index to the radioactive contamination of the sample.

REAGENTS

Ethyl alcohol: 95%
Nitric acid: 3N, concentrated

PROCEDURE

1. Filter a 1000-ml aliquot of the sample through a 9-cm Buchner funnel using a 9-cm diameter Whatman No. 42 filter paper. Collect the filtrate in a 2000-ml filter flask and save for step 3.

2. Place filter paper containing suspended solids in a tared planchet, saturate with ethyl alcohol, and ignite. Flame the planchet to a dull red, cool, weigh for self-adsorption correction, and submit for alpha and beta counting.

3. Transfer a 250-ml aliquot of the filtrate from step 1, or unfiltered sample, to a 400-ml beaker, add 10 ml nitric acid (concentrated) and evaporate to near dryness. Quantitatively transfer to a tared planchet using 3N nitric acid. Evaporate and flame planchet to a dull red. Cool, weigh for self-absorption correction, and submit for alpha

and beta counting. Volumes smaller than 250 ml may be used if weight is too large for efficient counting.

CALCULATIONS

Alpha or beta activity (pCi/liter)

$$= \frac{\text{cpm (dissolved solids)}}{2.22 \times \text{eff} \times \text{sample volume}} + \frac{\text{cpm (suspended solids)}}{2.22 \times \text{eff} \times \text{sample volume}}$$

where eff = beta counting efficiency as determined using a strontium-90/yttrium-90 equilibrium standard including self-absorption correction and alpha counting efficiency using plutonium-239

DISSOLUTION OF SAMPLES FOR RADIUM-226 ANALYSIS

PRINCIPLE OF THE METHOD

Since individual samples are not constant in their composition, methods or variations of methods must sometimes be used for a complete digestion of the sample. The following methods for the dissolution of environmental samples were prepared in the hope of aiding in the more rapid final analysis of samples and to avoid the trial and error methods for the dissolution of different samples.

REAGENTS

Hydrochloric acid: 3N
Hydrofluoric acid: 48%w
Hydrogen peroxide: 30%w
Sodium carbonate: C. P. grade granules
Sodium hydroxide: C. P. grade pellets
Nitric acid: 16N, 8N, 3N

APPARATUS

- Analytical balance
- Beakers, various
- Burner, blast
- Crucible, platinum, 30-ml
- Dish, evaporating, #0
- Filter paper, Whatman #42
- Hotplate
- Membrane filter and holder
- Muffle furnace

TOTAL DECOMPOSITION METHODS

See "Preparation of Nonhomogeneous Samples for Analysis," page 20.

1. If the sample ash appears light in color or white ash with no visible carbon:

   a. Transfer a weighed aliquot to a 400-ml beaker.

   b. Digest with 100 ml 3N nitric acid.

   c. Evaporate to near dryness, dissolve with precipitate with 3N nitric acid.

   d. If the sample solution is clear with no visible precipitate, adjust the volume to 150 ml with distilled water and proceed, using suitable radium method. (See "The Determination of Radium-226 in Environmental Samples by Radon Emanation," page 39.)

2. When the samples contain visible carbon or the samples have been digested in 3N nitric acid and show evidence of carbon:

   a. Add 15 ml of concentrated nitric acid.

   b. Evaporate to near dryness.

   c. Dilute the sample with concentrated nitric acid.

   d. Add a few ml of 30% hydrogen peroxide.

   e. Evaporate to near dryness and repeat steps c and d, if necessary, until solution is clear.

   f. If no visible precipitate remains, adjust volume to 150 ml with distilled water and proceed with suitable radium method. (See "The Determination of Radium-226 in Environmental Samples by Radon Emanation." page 39.)

3. When obviously large amounts of carbon remain in the sample:

   a. Transfer a weighed aliquot to a #0 Coors evaporating dish.

   b. Wet the sample with concentrated nitric acid.

c. Place the evaporating dish in a cold muffle furnace and slowly increase the temperature to 400° C. Repeat acid and heat if necessary.

d. Cool, dissolve the ash with 8N nitric acid.

e. Transfer the sample to a 400-ml beaker using 3N nitric acid.

f. If no visible precipitate remains, adjust the volume to 150 ml with distilled water and proceed using a suitable radium method. (See "The Determination of Radium-226 in Environmental Samples by Radon Emanation," page 39.)

4. When the sample has been dissolved in nitric acid and a visible residue remains:

a. Filter the sample through a #42 Whatman filter paper.

b. Return the filtrate to the 400-ml beaker.

c. Transfer the filter paper with precipitate to a 30-ml platinum crucible.

d. Place platinum crucible in the muffle furnace until paper is ashed.

e. Cool, add a few mls of 48% hydrofluoric acid and take to dryness on the hot plate.

f. Repeat step e.

g. Dissolve the residue with concentrated nitric acid, and take to dryness on the hot plate. Repeat.

h. Cool, dissolve the remaining residue with 3N nitric acid, swirl the platinum crucible to be sure of washing any remaining residue from the sides of the crucible.

i. Transfer the solution to original beaker, washing the platinum crucible with 3N nitric acid.

j. Adjust the volume of the sample to 150 ml with distilled water and proceed with suitable radium method. (See "The Determination of Radium-226 in Environmental Samples by Radon Emanation," page 39.)

DETERMINATION OF RADIUM-226
IN ENVIRONMENTAL SAMPLES BY RADON EMANATION

PRINCIPLE OF THE METHOD

A weighed aliquot of sample ash is digested with 16N nitric acid and 30% hydrogen peroxide. After addition of barium carrier, the sample is precipitated as a carbonate with ammonium carbonate. The carbonate precipitate is dissolved with 3N nitric acid and the sample is precipitated as a chromate using ammonium chromate. The chromate precipitate is dissolved with 12N hydrochloric acid, and reprecipitated as a chloride with hydrochloric acid-ether solution. The chloride precipitate is readily soluble in less than 10 ml water. The solution is then transferred to an emanation tube for 28 days.

REAGENTS

Acetic acid: 6N
Alcohol-hydrochloric acid: 10 ml hydrochloric acid/100 ml absolute alcohol
Ammonium acetate: 6N
Ammonium carbonate: saturated solution
Ammonium carbonate wash solution
Ammonium dichromate: 0.1M, 1.0M
Ammonium hydroxide: 6N, 15N
Barium carrier: 1 mg barium/ml, 10 mg barium/ml
Hydrochloric acid: 12N
Hydrochloric acid-ether
Hydrogen peroxide: 30%w
Nitric acid: 3N, 16N

APPARATUS

Bath, ice
pH meter
Tube, immersion, Corning #39535, 20M or equivalent
Tube, emanation (Figure 5)

PROCEDURE

See "Dissolution of Samples for Radium-226 Analysis," page 36.

1. Weigh on analytical balance a 5-gram portion of sample ash into a 400-ml beaker.

2. Digest with 16N nitric acid and 30% hydrogen peroxide, evaporate to near dryness, repeat the digestion if necessary until sample is in solution. Do not allow sample to evaporate to dryness.

3. Increase volume to at least 150 ml with distilled water, heat and add a few ml 16N nitric acid to insure complete solution of the sample. (Some flocculent precipitate of phosphates may be present and may be disregarded at this time.)

4. Add 5 mg barium carrier and ammonium hydroxide until precipitate forms. Add 30 ml saturated solution of ammonium carbonate, allow precipitate to settle for at least 30 minutes. Filter using immersion tube, or centrifuge using a 250-ml centrifuge bottle. Discard the supernate and wash the precipitate several times with hot ammonium carbonate wash solution.

5. Dissolve the carbonate precipitate with 3N nitric acid, wash the filter stick (or centrifuge tube) and walls of the beaker with 3N nitric acid.

6. Add 100 mg of barium carrier, increase the volume of the sample to 150 ml with distilled water, heat on the hot plate until the sample is in solution.

7. Adjust the pH to 4.2 to 4.6 with 6N ammonium hydroxide or 3N nitric acid. Add 3 ml 6N acetic acid, 10 ml ammonium acetate and slowly, with stirring, add 10 ml 1.0M ammonium dichromate solution pH 6.5. Allow the chromate precipitate to settle for a minimum of 30 minutes. Filter, using an immersion stick, or centrifuge using a 250-ml centrifuge bottle. Discard the filtrate and wash the precipitate with 0.1M solution of ammonium dichromate pH 6.5.

8. Dissolve the precipitate with 12N hydrochloric acid, wash the sides of the beaker and the filter stick with 12N hydrochloric acid. Heat on the hot plate and add more hydrochloric acid if necessary to insure complete solution of the sample.

9. Remove the sample from the hot plate and chill in an ice bath. In a hood, add 30 ml hydrochloric acid-ether solution (CAUTION, HIGHLY FLAMMABLE). Allow sample to set in ice bath for 20 minutes. Filter using a filter stick that has been washed with hydrochloric acid-ether solution. Discard the filtrate and wash the barium (radium) chloride precipitate with absolute alcohol-hydrochloric acid solution.

10. Dissolve the barium (radium) chloride with a maximum of 8 ml of distilled water. Transfer the sample to an emanation tube (Figure 5), wash beaker, and funnel with a maximum of 4 ml distilled water. Final volume should be no less than 10 ml and no more than 12 ml. Seal and allow to ingrow for 28 days. (See "The Apparatus and Method for Radon Transfer," page 48, for de-emanation of radon.)

CALCULATIONS

Radium-226 (pCi/liter or kilogram)

$$= \frac{\text{cpm}}{\text{cell factor} \times \text{sample weight or volume}}$$

THE DETERMINATION OF RADIUM-226 IN WATER SAMPLES BY RADON EMANATION

(Rushing 1964)

PRINCIPLE OF THE METHOD

An aliquot of the water sample is transferred to a 2-liter beaker. The radium is co-precipitated as a sulfate using a lead carrier. The lead-radium sulfate is reprecipitated as a carbonate. The carbonate precipitate is then dissolved in 3N nitric acid, transferred to a radon bubbler, and allowed to ingrow for 28 days.

REAGENTS

Ammonium acetate: 6M
Lead nitrate carrier: 100 mg lead/ml
Nitric acid: 3N, 16N
Sodium carbonate: 3N
Sulphuric acid: 1N, 18N

APPARATUS

Hot plate, stirrer, magnetic, with stir bars
pH meter
Tube, radon emanation (Figure 5)

Rushing, D. E., et al. The Analysis of Effluents and Environmental Samples from Uranium Mills and of Biological Samples for Radium, Polonium and Uranium. Rad. Hlth & Safety in Mining and Milling of Nuclear Materials II:187 (1964), International AEC, Vienna, Austria.

PROCEDURE

1. Transfer a 1500-ml aliquot of the sample to a 2-liter beaker.

2. Adjust the pH to approximately 1.0 with concentrated nitric acid, add 10 ml lead carrier.

3. Add 100 ml 18N sulfuric acid, and heat to about 70° C with stirring on the magnetic stirrer hot plate.

4. Remove the sample from the stir plate and allow precipitate to settle overnight. Decant, discard the supernate and transfer the precipitate to a 40-ml centrifuge tube using 1N sulfuric acid.

5. Centrifuge, discard the supernate. Wash the precipitate with 10 ml of water, centrifuge, discard the supernate.

6. Rinse the walls of the 2-liter beaker with 5 ml 6M ammonium acetate. Transfer this solution to the precipitate in the centrifuge tube. Bring the volume in the centrifuge tube to about 20 ml with 6M ammonium acetate.

7. Heat in a water bath with stirring until the precipitate dissolves.

8. Slowly add 20 ml 3N sodium carbonate, continue heating, and stir for 15 minutes. Centrifuge, discard the supernate.

9. Dissolve the carbonate precipitate with 10 ml 3N nitric acid, reprecipitate using 30 ml hot 3N sodium carbonate.

10. Heat and stir for approximately 15 minutes, centrifuge, discard the supernate.

11. Dissolve the carbonate precipitate with 5 ml 3N nitric acid, transfer the sample to a radon bubbler (Figure 5) with a maximum of 7 ml of distilled water.

12. Seal the bubbler and allow the sample to ingrow for 28 days before counting. (See "The Apparatus and Method for Radon Transfer," page 48, for de-emanation of radon.)

THE ANALYSIS OF RADIUM-226 IN SOIL, ORES AND MILL TAILINGS

PRINCIPLE OF THE METHOD

This procedure describes a method for the determination of radium-226 in soil, ore, mill tailings, sludge, air filters, feces, and urine ash. (See "Dissolution of Sample for Radium-226 Analyses," page 36.) A suitable sample is transferred to a platinum crucible, mixed with Nicholson's flux and fused. The fused cake is dissolved in sulfuric acid and barium carrier is added. The barium sulfate is heated with phosphoric acid to form the acid soluble phosphate. The cooled barium phosphate is dissolved in hydrochloric acid and transferred to an emanation tube.

REAGENTS

Ammonium Sulfate: 10%w
Barium carrier: 10 mg/ml
Hydrochloric acid: 3N, 6N
Hydrofluoric acid: 48%w
Hydrogen peroxide: 3%w
Nicholson's flux
Phosphoric acid: concentrated
Sulfuric acid: concentrated, 0.5%

APPARATUS

Burner
Crucible, platinum, 30-ml
Emanation tube (Figure 5)

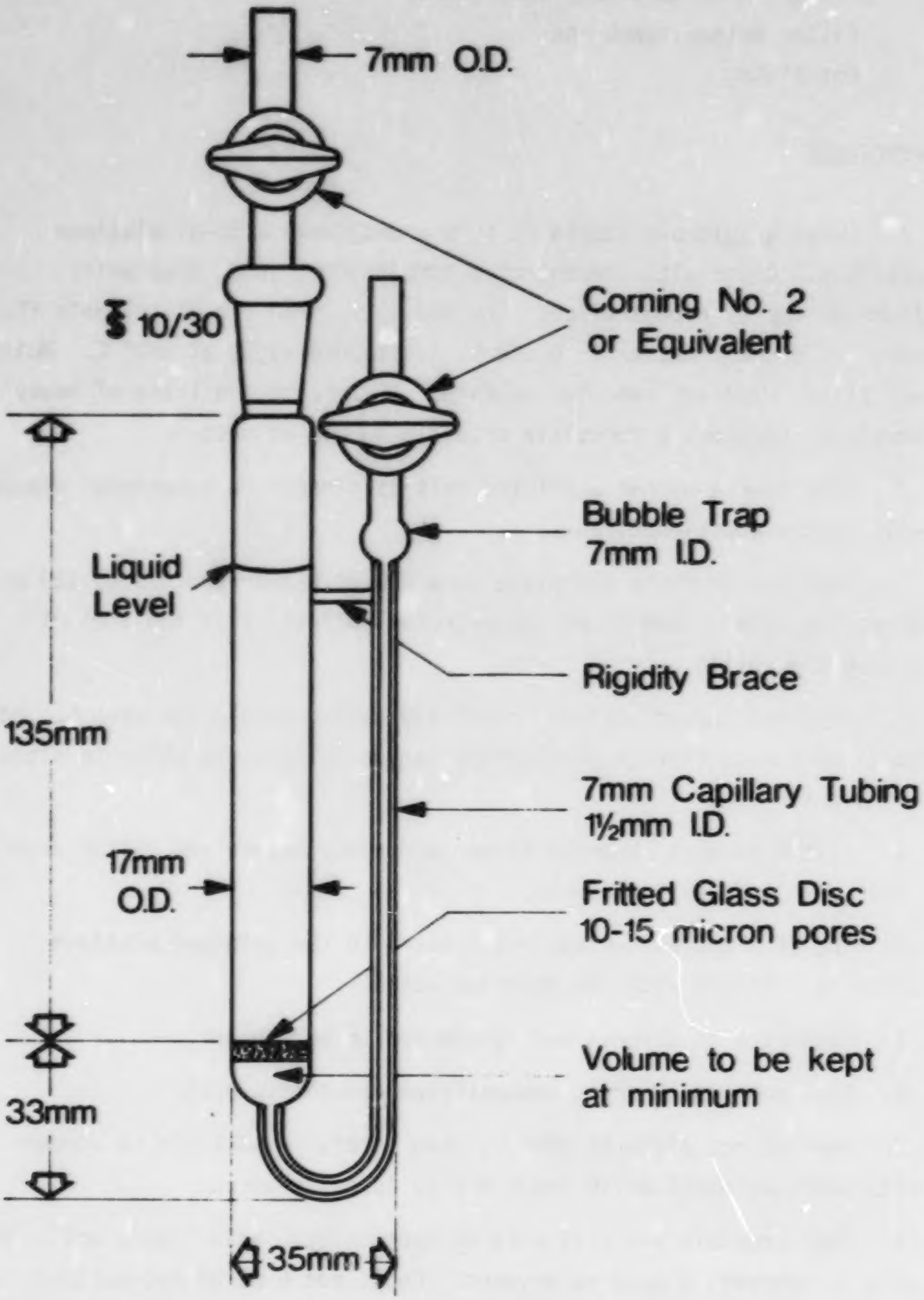

7mm O.D.
Corning No. 2
or Equivalent
10/30
Bubble Trap
7mm I.D.
Liquid
Level
Rigidity Brace
135mm
7mm Capillary Tubing
1½mm I.D.
17mm
O.D.
Fritted Glass Disc
10-15 micron pores
Volume to be kept
at minimum
33mm
35mm

Figure 5. Emanation Tube (Bubbler)

Filter, membrane, Hawp 04700, 0.5μ
Filter holder, membrane
Hot plate

PROCEDURE

1. Weigh a suitable sample (1 to 5 grams) into a 30-ml platinum crucible. Cover with concentrated hydrofluoric acid, heat until fluoride fumes, repeat twice. Dry and cool. Add 8 g Nicholson's flux mix. If organic matter is present, ignite overnight at 500° C. Moisten air filter with 10% ammonium sulfate. If more than a trace of heavy metals is present, a porcelain crucible should be used.

2. Fuse over a burner until the melt is clear. An occasional sample will requre additional flux.

3. Cool the crucible and place in a 250-ml beaker containing 120 ml distilled water. Add 20 ml concentrated sulfuric acid and 5 ml 3% hydrogen peroxide.

4. When melt has dissolved, rinse and save crucible for step 6. Add 10 ml barium carrier to precipitate barium sulfate and allow to stand overnight.

5. Filter through membrane filter and rinse beaker and filter several times with 0.5% sulfuric acid.

6. Transfer the filter and precipitate to the original platinum crucible. Dampen with 10% ammonium sulfate.

7. Evaporate to dryness and ignite over blast burner.

8. Cool and add 20 drops concentrated phosphoric acid.

9. Heat on hot plate at 200° C, then carefully heat over a burner with swirling until white fumes are no longer evolved.

10. Cool crucible and fill with 6N hydrochloric acid. Warm until free acid is removed, almost to dryness. Cool, add 6 ml 3N hydrochloric acid, heat to dissolve, and cool.

11. Transfer the solution to an emanation tube (Figure 5) with distilled water. Volume should be 10-12 ml.

12. Seal and allow to ingrow for 28 days. (See "The Apparatus and Method for Radon Transfer," page 48, for de-emanation of radon.)

CALCULATION

$$\text{Radium-226 (pCi/liter or gram)} = \frac{\text{cpm}}{\text{F} \times \text{sample size (in liters or grams)}}$$

where $$\text{F} = \frac{\text{cpm of standard}}{\text{pCi of standard}}$$

This is a factor that includes the counting efficiency and chemical efficiency of the method. It is determined by preparing similar type standards, i.e., adding a known amount of radium-226 to low-level bone ash, food ash, etc. After chemical separation of the radium and 30 days radon ingrowth, the standard is transferred and counted at the same time as the unknown.

THE APPARATUS AND METHOD FOR RADON TRANSFER

PRINCIPLE OF THE METHOD

The object of this procedure is to describe the apparatus and method necessary to transfer the radon-222 gas produced in the solution containing the radium-226 to the scintillation chamber.

Many variations of the procedure and apparatus described herein could be used; however, the system has been used for routine analysis and it has proved to be satisfactory.

REAGENT

Air, compressed (hold for 90 days before using)

APPARATUS

The specification for the transfer apparatus is illustrated in Figure 6. The use of glass joints with O-ring seals is recommended because the O-ring seals decrease the amount of stopcock grease necessary to seal the joints.

PROCEDURE

1. Attach a scintillation chamber to the manometer by means of a flat, O-ring, sealed glass joint.
2. Attach a bubbler tube containing the sample solution to an Ascarite-Drierite drying tube with a short length of rubber tubing. The drying tube is attached to a short length of thermometer tubing with rubber tubing.

3. Stopcock 1 is opened and a vacuum is applied to the system.

4. When the right-hand leg of the U-tube manometer has reached its maximum height, close stopcock 1.

5. The system should be left in this configuration for three to five minutes. If the mercury begins to drop in the right-hand leg of the manometer, check the glass joints and rubber tubing connections for leaks. Apply a very light coating of Dow-Corning silicon grease to the connections if necessary, then repeat steps 4 and 5.

6. Open stopcocks 1 and 2 and permit the mercury in the right-hand leg of the manometer to reach its maximum height. Close stopcock 1 and check for leaks as in step 5.

7. Connect the dry aged air tank with gum rubber tubing. The air pressure should be limited to one or two pounds of pressure. A needle valve between the air tank regulator and the bubbler is recommended.

8. Open stopcock 3 slowly to prevent a pressure surge. Open stopcock 4 using the same precaution.

9. The air pressure will have to be increased occasionally to keep the flow through the bubbler fairly constant.

10. The flow of aged air through the bubbler should be controlled so that the transfer reaches completion within 25-30 minutes.

11. The mercury in the right-hand leg of the manometer will begin to drop as the air is passed through the bubbler. When the level of the mercury in both legs of the manometer is equal, shut off stopcocks 4, 3, and 2 in that order.

12. Remove the scintillation chamber and place in a light-tight cabinet for the 6-hour ingrowth period.

13. Remove the purged bubbler and desiccant. The system is ready now for the next sample.

CALCULATIONS

$$\text{Radium-226 (pCi/unit)} = \frac{\text{cpm}}{\text{C.F.} \times \text{sample weight or volume}}$$

where cpm = gross counts divided by counting time - background

C.F. = cell factor determined by de-emanating a standard solution. It includes all conversion factors.

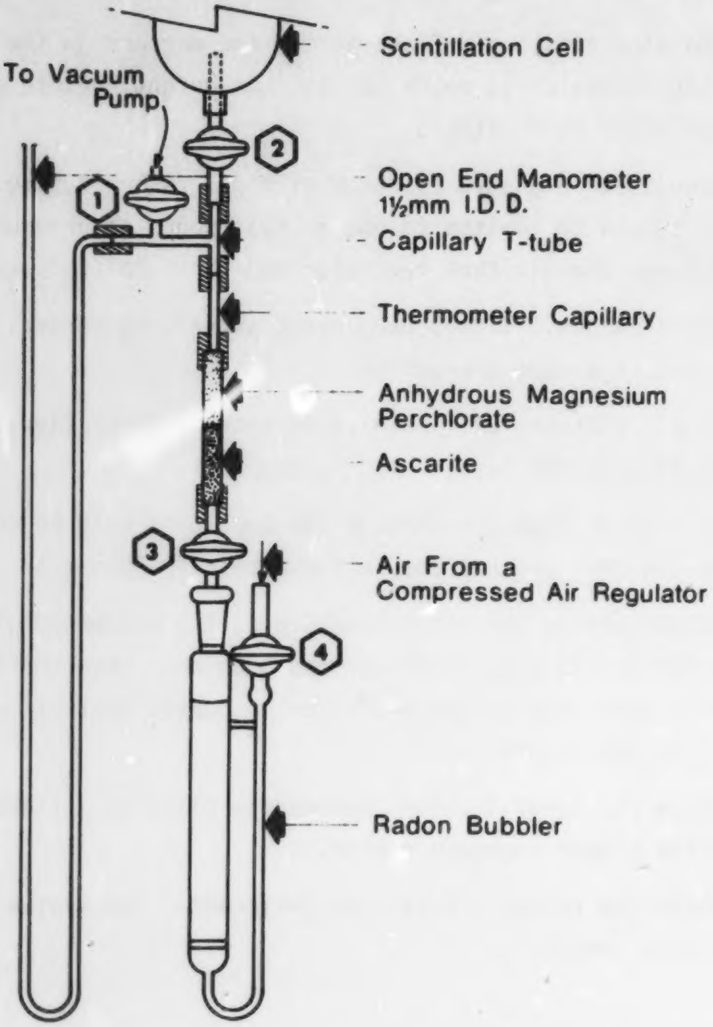

Scintillation Cell
To Vacuum Pump
②
Open End Manometer 1½mm I.D.D.
①
Capillary T-tube
Thermometer Capillary
Anhydrous Magnesium Perchlorate
Ascarite
③
Air From a Compressed Air Regulator
④
Radon Bubbler

Figure 6. Apparatus for Radon Transfer

RADON IN ATMOSPHERIC SAMPLES
AND NATURAL GAS

PRINCIPLE OF THE METHOD

This method describes a procedure for the separation and collection of radon from atmospheric samples and natural gas. Air samples as received are of two types: a "grab" sample of 1 or 2 liters and an integrated sample representing 48 hours of sampling. Natural gas samples are analyzed as in Procedure B. All of the "grab" sample or a portion of the integrated sample is transferred to the gas separation apparatus. The sample is passed through a carbon dioxide and water removal trap, then through two charcoal traps at dry-ice acetone temperature. The radon is emanated with helium and collected in scintillation cells.

REAGENTS

Ascarite
Charcoal
Drierite

APPARATUS

See Figure 7
T_1 - steel ball trap
D_1 - Ascarite and Drierite
C_1 - charcoal
C_2 - charcoal

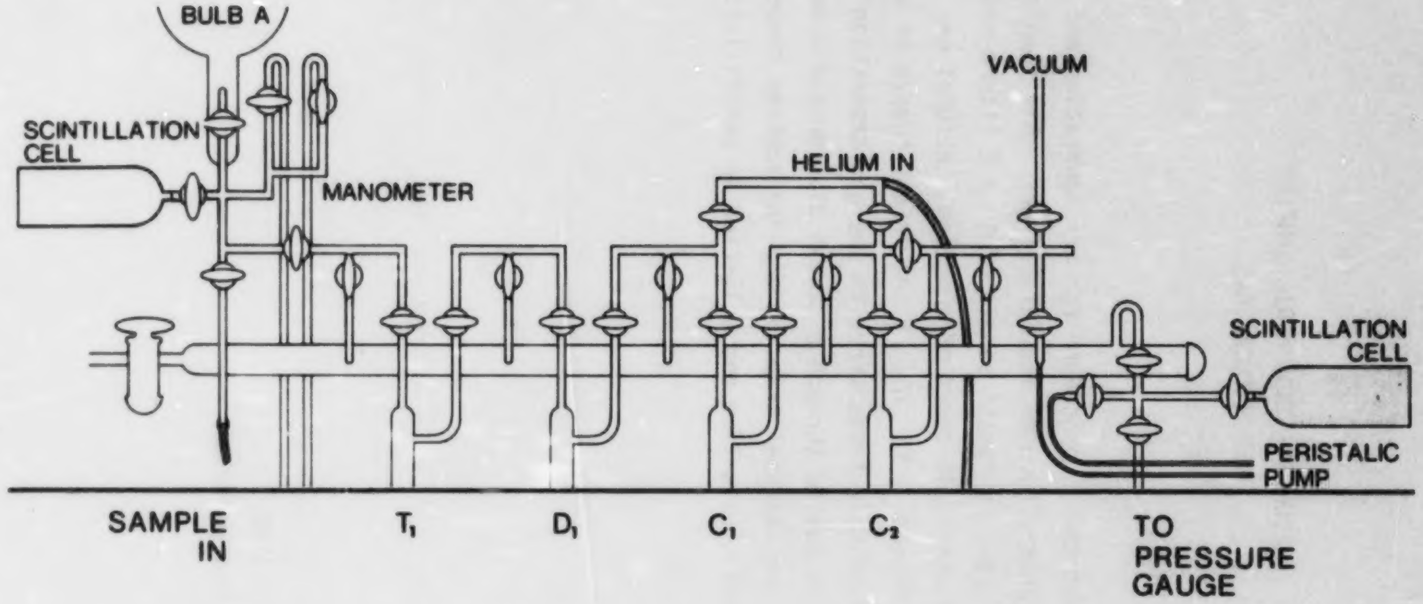

BULB A
SCINTILLATION CELL
MANOMETER
HELIUM IN
VACUUM
SCINTILLATION CELL
PERISTALIC PUMP
SAMPLE IN
T_1
D_1
C_1
C_2
TO PRESSURE GAUGE

Figure 7. Apparatus for Radon in Air

PROCEDURE

A. For Air

1. Attach sample container to the sample-in line (Figure 7) and evacuate all lines, bulb A, and scintillation cell. Record room pressure and temperature.

2. Transfer all of the "grab" sample into bulb A, or bring bulb A to atmospheric pressure with the integrated sample. Record pressure and temperature.

3. Fill scintillation cell, located at B (Figure 7) with sample and record pressure and temperature.

4. Immediately count scintillation cell for 30 minutes. If count rate is 0.3 cpm or greater, make a duplicate as in step 3. Continue counting repeatedly at 30-minute counting times until the ingrowth of the radon daughters is complete, approximately 4½ hours.

5. If the count rate is less than 0.3 cpm, continue as in step 6.

6. With T_1 in ice water, D_1 at room temperature, C_1 and C_2 in dry ice acetone (DIA), establish flow bulb A $\rightarrow T_1 \rightarrow D_1 \rightarrow C_1 \rightarrow C_2 \rightarrow$ vacuum.

7. Continue flow until pressure in bulb A returns to original pressure (approximately 10 minutes).

8. Close all stopcocks and turn off vacuum pump. Remove DIA from C_1 and replace with a furnace preheated to 350° C.

9. Establish flow helium in C_1 → peristalic pump → first scintillation cell. Pump for 1 minute.

10. Turn off pump, open helium valve and allow helium to mix in C_1 for one minute.

11. Repeat procedure steps 6 and 7, five times.

12. Establish flow helium in C_2 → peristaltic pump → second scintillation cell. Remove ice water and replace with 400° C furnace. Pump for one minute.

13. Turn off pump, open helium valve and allow helium to mix in C_2 for one minute.

14. Repeat steps 10 and 11 five times.

15. Place cells in radon counting apparatus and count at 30-minute intervals until the ingrowth of the radon daughters is complete.

B. For Natural Gas

1. Attach sample bottle to Sample In with an Ascarite-Drierite drying tube in line.

2. Evacuate all transfer lines and scintillation cells. Close vacuum valve and check for leaks. (A movement of mercury in manometer will indicate a leak.)

3. When transfer system is leak-free, gradually open regulator valve and transfer sample to three-scintillation cells.

4. When pressure in the cell reaches atmospheric pressure (as indicated on the manometer), close all valves and record pressure and temperature.

5. Remove scintillation cells for alpha counting, as in step 15, Procedure A.

PROCEDURE FOR THE SEPARATION OF RADIOKRYPTON, RADIOXENON AND METHANE IN ATMOSPHERIC SAMPLES

PRINCIPLE OF THE METHOD

A method is described to separate krypton, xenon, and methane from atmospheric samples. A sample of one cubic meter will suffice. Detectable limits for this size sample are 2 pCi/cubic meter. Water and carbon dioxide are removed in a molecular sieve trap. The noble gases are adsorbed of charcoal at liquid nitrogen temperatures and separated on molecular sieve columns.

REAGENTS

Acetone
Alcohol bath: -32° C
Charcoal, coconut: 16-20 mesh
Dry ice
Helium
Krypton carrier
Liquid nitrogen
Liquid scintillation cocktail
Molecular sieve 5A: 30-60 mesh
Molecular sieve 13X: 1/8" x 3/16" pellets
Water baths, 20° C and 100° C
Xenon carrier

APPARATUS

From left to right in Figure 8 the various components of the apparatus are:

Mol-Sieve 13x - 40 mm ID trap packed with 200 grams 1/8-inch x 3/16-inch pellets of molecular sieve 13X

Pre-cooler - 150 cm of 12 mm OD glass tubing

Pressure gauge - differential manometer

FM, and FN_2 - flow meters

C_1 - 40 mm ID trap packed with 100 grams 16-20 mesh activated charcoal

MS, and MS_2 - 150 cm of 12 mm OD tubing packed with 30-60 mesh molecular sieve 5A

V-13 - a Varian two-position, six-part linear gas sampling valve

C_2 - 20 cm length of 1/8-inch copper tubing packed with 0.3 g 30-50 mesh activated charcoal

Liquid Scintillation Vial - 20 ml liquid scintillation with Luer joint and valve

Manometer - Digital manometer 0-100 mm of Hg

It is not possible to show on the line drawing all the valving and vacuum connections necessary for the operation. However, a purified helium supply is connected at both the flow meters, and vacuum, provided by a mechanical vacuum pump, is provided at both vacuum connections.

Thermistors, located in the outlets of C_1, MS, and MS_2, are used to detect the gas elution. Figure 8 illustrates the wiring diagram for the detection circuit. The thermistor detector unbalances a Whetstone bridge circuit which in turn drives a pen on a recorder. A continuous record of the location of the various gases is then maintained throughout the separation. Various other pieces of hardware are necessary to affect the separations: electric furnaces capable of attaining 350° C, a temperature indicator, a 500-watt immersion heater, and several 500- and 1000-ml Dewar flasks.

PREPARATION OF APPARATUS

Degas traps at 350° C and evacuate until a pressure of $<10^{-4}$ mm of Hg is obtained. Then fill traps with helium and zero the thermistor cells with a flow of helium. Cool the pre-cooler, C_1, MS, and MS_2 with liquid nitrogen (LN).

SAMPLE TRANSFER

Because of the difference in sampling technique, the transfer of the sample will be treated separately:

A. Grab. Record the weight and pressure of the sample bottle. Connect the bottle to the sample inlet port and place in a heating mantle. Using a roughing vacuum pump on exit from C_1 and suitable valving, establish sample flow through T_1 and C_1 of about 15 liters/min and 35-cm pressure. (Reduced pressure is necessary to avoid condensation of liquid air in system.) Continue bleeding sample into T_1 and C_1 until the pressure drops to less than 10 mm helium. Shut off sampling inlet port and add the carriers. Record transfer time (about 20-30 minutes).

B. Cryogenic. Remove the sampler from the LN Dewar and place in a furnace capable of reaching 350° C in 45 minutes, attach helium line to inlet of sampler and outlet to sample inlet port. After checking for leaks, with suitable valving use needle value on helium to establish flow through T_1 and C_1 of 15-20 liters/min at 35-cm helium pressure with roughing pump. Continue adding sample until the molecular sieve container is at 350° C. Hold for 30 minutes, shut helium valve and sample port, and add carriers. Record transfer time (from 1½ to 2 hours). At this point, T_1 contains water and carbon dioxide. C_1 contains carbon dioxide, krypton, xenon, oxygen, and nitrogen.

C. Integrated. Record the weight and pressure of the sample bottle. Connect the sample bottle to the sample inlet port. Using the vacuum pump on the exit from C_1, and suitable valving, establish sample flow through molecular sieve, pre-cooler, and C_1 of about 15 liters/min and 35-cm absolute pressure. Continue bleeding sample into C_2 until the pressure drops to less than 10 mm of mercury. Shut off sampling inlet port. As the sample has had 1 ml stable xenon carrier added before sampling and the one cubic meter of air contains 1 ml stable krypton and methane, no further carriers need be added.

PROCEDURE

A. Water Removal and Recovery

1. Collect the water and carbon dioxide in the molecular sieve trap (these may be recovered by heating). This procedure is described in Section E, page 77.

B. Removal of Air from C_1

2. Close valves C and B, open tube D_1 with C_1 in LN, establish helium flow (600-800 ml/min) through C_1, thermistor 1 and vent. Remove LN from C_1 and replace with dry ice acetone (DIA) slush. Continue this flow until all the air is removed as evidenced by a return of the pen recorder to the base line (approximately 55 minutes). Shut vent valve and helium flow.

C. Removal of Krypton, Xenon, and Methane from C_1

3. Leave DIA on C_1 and re-establish helium flow $C_1 \rightarrow$ thermistor 1 $\rightarrow$ $MS_1 \rightarrow$ vent 2. MS_1 and MS_2 are in LN when flow is stabilized. Remove DIA from C_1 and replace with electric furnace and start heating.

4. Continue heating until a temperature of 350° C is reached or until all of the gases are transferred to MS_1. This is indicated by a return to base line by the recorder. (A shift in base line is usually noted at this point due to the higher temperature of the gases entering the thermistor and also a decrease in flow rate.)

5. Shut vent and turn off helium flow. Open high vacuum valve to C_1 and continue heating until a temperature of 350° C is reached and a vacuum of less than 10^{-4} mm helium is obtained. (C_1 is then ready for another run.)

D. Separation of Krypton, Xenon, and Methane from MS_1

6. With LN on MS_1 and MS_2, establish helium flow (200-300 ml/min) $MS_1 \rightarrow$ thermistor 2 $\rightarrow$ vent 2.

7. Remove LN from MS_1 and replace with a -32° C alcohol bath. After approximately two minutes, a sharp increase is noted on the recorder. This is the argon and oxygen. Continue helium flow until the pen returns to base line (4-5 minutes).

8. Rearrange helium flow, $MS_1 \rightarrow MS_2 \rightarrow$ vent. Continue flow until the krypton is eluted from MS_1 (approximately 12-14 minutes).

9. Quickly rearrange flow $MS_1 \rightarrow$ vent (MS_2 and vent closed). Replace the alcohol on MS_1 with cold water (20° C) and elute nitrogen to vent. Watch the elution of nitrogen carefully, and by rearranging the flow $MS_1 \rightarrow MS_2 \rightarrow$ vent, transfer the last of the nitrogen peak to MS_2 (this is mostly methane).

10. Place immersion heater in cold bath and heat unit until the carbon monoxide and xenon are all transferred to MS_2 (approximately 10 minutes). Remove boiling water from MS_1.

E. Separation and Collection of Krypton, Methane and Xenon from MS_2

11. Prepare C-2 by heating with a heat gun. Place a clean liquid scintillation vial and valve in position. Evacuate to 0.0 mm on the manometer. Place LN on C-2.

12. Arrange helium flow $MS_1 \rightarrow MS_2 \rightarrow$ thermistor 3 → vent. Remove LN from MS_2 and replace with -32° C alcohol bath. The small oxygen peak is noted in 2 minutes. When the krypton peak appears immediately close vent 3 and open V-13. Collect the krypton in C-2 until the pen or the recorder returns to base line. Close V-13, open vent 3 and allow helium to continue to flow.

13. Remove the helium in C-2 by evacuating until a pressure <0.1 mm of Hg is attained. Close vacuum valve and heat C-2 to transfer the krypton to the vial. When pressure has stabilized, record pressure and temperature.

14. Prepare C-2 by heating with a heat gun. Place a clean liquid scintillation vial and valve in position. Evacuate to 0.0 mm on the manometer. Place LN on C-2.

15. Flow should still be $MS_1 \rightarrow MS_2 \rightarrow$ thermistor 3 → vent 3. Replace alcohol bath with cold water. A small peak of nitrogen will be noted on the recorder. When the methane peak appears, immediately close vent 3 and open V-13. Collect the methane in C-2 until the recorder pen returns to the base line. Close V-13, open vent 3 and allow helium to continue to flow.

16. Transfer the methane to the vial as in steps 12 and 13.

17. Prepare C-2 by heating with a heat gun. Place a clean liquid scintillation vial and valve in position. Evacuate to 0.0 mm on the manometer. Place LN on C-2.

18. Flow should still be $MS_1 \rightarrow MS_2 \rightarrow$ thermistor 3 → vent 3. Heat MS_2 with immersion heat. Allow the carbon monoxide peak to vent and immediately close vent 3, open V-13. Collect the xenon in C-2 as in steps 12 and 13.

19. Transfer the xenon to vial as in steps 12 and 13.

CALCULATIONS

1. $$V_1 = \frac{1.14 \times \text{sample weight}}{1293}$$

where V_1 = volume krypton in sample

1.14 = volume concentration of krypton in air

1293 = grams of air per cubic meter

2. $$\text{Volume of } V_{Kr}, V_{Xe}, \text{ or } V_{^{14}C} \text{ recovered} = v \times \frac{p}{760} \times \frac{273}{t + 273}$$

where v = vial volume + volume of C-2 and transfer line

p = vial pressure

t = temperature in °C

3. $$\text{Kr recovered (0/0)} = \frac{V_{Kr}}{V_1} \times 100$$

4. $$\text{Xe recovered (0/0)} = \frac{V_{Xe}}{V_3} \times 100$$

where V_3 = volume xenon added

5. $$\text{CH}_4 \text{ recovered } (0/0) = \frac{V_{CH_4}}{V_4} \times 100$$

where V_4 = volume of methane in sample

6. Kr, Xe, or CH_4 (pCi/m^3)

$$= \frac{\text{cpm}}{2.22 \times \text{CE} \times \text{volume gas in vial} \times \text{sample size}}$$

where CE = fractional counting efficiency

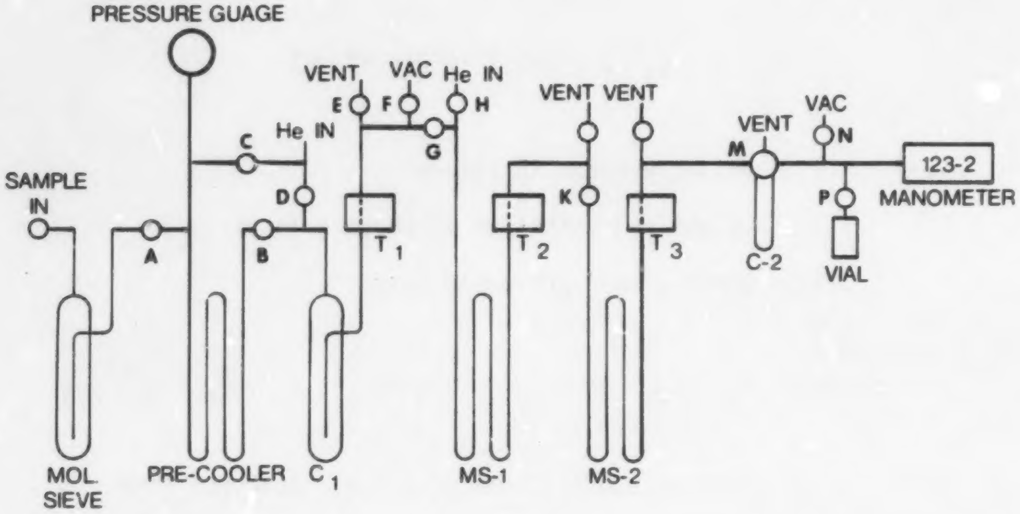

PRESSURE GUAGE
VENT
VAC
He IN
E
F
H
G
C
He IN
D
SAMPLE IN
A
B
T 1
VENT VENT
T 2
K
T 3
VENT
M
VAC
N
123-2
P
MANOMETER
C-2
VIAL
MOL. SIEVE
PRE-COOLER
C 1
MS-1
MS-2

Figure 8. Flow Diagram for Separation of Methane, Krypton, and Xenon

DETERMINATION OF TRITIUM IN WATER

PRINCIPLE OF THE METHOD

A portion of the water sample is distilled to remove the water from any dissolved or suspended solids. Aliquots of distillate are pipetted into counting vials together with a liquid scintillation solution. The sample is then counted in a liquid scintillation spectrometer. A standard tritium sample is counted for efficiency determination and a low-tritium water sample is counted for background. Radioiodine interferes but may be eliminated by distillation over silver nitrate.

REAGENTS

Liquid scintillation solution
Tiritum standard, National Bureau of Standards

APPARATUS

Pipet, 5-ml, 20-ml
Spectrometer, liquid scintillation
Vial, polyethylene, screw cap, 25-ml

PROCEDURE

1. Distill a 10-50 ml portion of the water sample just to dryness. Vent the first steam and collect the distillate in a cold trap. If radioiodine is present add 0.1 g silver nitrate crystals and distill. (Note a)

2. Pipet a 5-ml portion of the distillate into the polyethylene counting vial (Note b) together with 20 ml of the liquid scintillation solution.

3. Make a background sample by pipetting a 5-ml portion of low-tritium water (Note c) into a vial containing 20 ml of liquid scintillation solution.

4. Make a standard sample by pipetting a 5-ml portion of a diluted National Bureau of Standards standard into a vial containing 20 ml of liquid scintillation solution.

5. Place the unknown, background, and standard samples in the liquid scintillation spectrometer. After the solutions have dark-adapted, usually about 48 hours, count for 100 minutes each. (Note d)

Notes: a. Vacuum distillation removes the water from dissolved solids which may be a source of contamination or could cause further quenching of the liquid scintillation process. (A thermal distillation may be used in place of vacuum.)

b. The polyethylene vials are used because they provide a higher counting efficiency and lower background than glass.

c. The low-tritium water used was obtained by distilling fossil water removed from an oil well.

d. The standard sample may be used to correctly set the upper and lower discriminators of the spectrometer.

CALCULATION

$$\text{Tritium (pCi/liter)} = \frac{1000A}{2.22BC}$$

where 1000 = ml/liter

A = net cpm

2.22 = dpm/pCi

B = fractional counting efficiency

C = sample volume

REMOVAL OF WATER FROM BLOOD, MILK, AND URINE FOR TRITIUM DETERMINATION

PRINCIPLE OF THE METHOD

This procedure describes a method for the determination of low levels of tritium in blood, urine, and milk. Benzene is added to the sample to form a low boiling azeotrope. The distillate, containing 99.93% water in the lower phase, is collected and the phases allowed to separate. The water phase is analyzed for tritium. Radioiodine and other volatile radionuclides interfere but may be eliminated (see "Determination of Tritium in Water," page 63).

REAGENTS

Antifoam A Dow Corning
Benzene (reagent grade)
Liquid scintillation solution
Molecular sieve 13X: 1/8-inch × 3/16-inch pellets

APPARATUS

Figure 9 illustrates the typical distillation apparatus. It consists of:

Condenser, West 200 mm
Distilling receiver, Barrett CGW #3622
Drying tube
Flask, round bottom, 1 neck T/S 24/40 joint
Heating mantle
Transformer, variable

PROCEDURE

1. Add 50 ml of sample, and 50 ml of benzene to boiling flask. Assemble apparatus as illustrated in Figure 9, with drying tube on vent of condenser.

2. Bring to boiling and collect distillate. Continue distillation until 15-20 ml of water is collected.

3. Allow phases to separate and the water phase to clear.

4. Transfer water portion to vial and proceed as in "Determination of Tritium in Water," page 63.

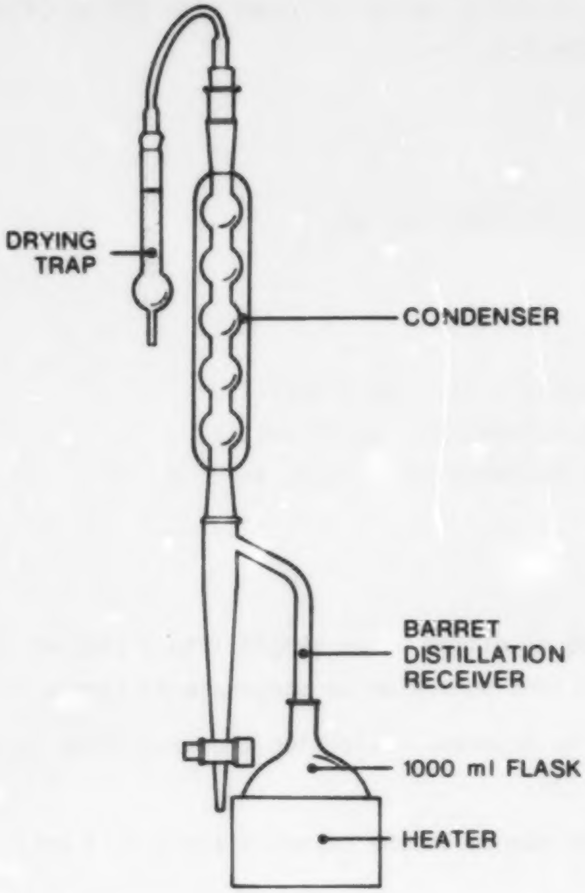

DRYING TRAP
CONDENSER
BARRET DISTILLATION RECEIVER
1000 ml FLASK
HEATER

Figure 9 Distillation Apparatus

DETERMINATION OF LOW LEVEL TRITIUM IN WATER
(ALKALINE ELECTROLYTIC ENRICHMENT)

PRINCIPLE OF THE METHOD

Distilled water samples with added sodium hydroxide are slowly electrolyzed at a constant temperature and rate. The hydrogen atom is preferentially evolved leaving the tritium atom behind. A lower level of detection of 2-3TU can be obtained with 250 ml of water sample and 18 days of electrolysis.

REAGENT

Sodium hydroxide: pellets

APPARATUS

Electrolytic cell. See Figure 10.
Constant current D.C. power supply
Constant temperature bath, 5° to 7° C

PROCEDURE

1. Place 500 ml of the water sample into a 1000-ml round bottom flask and add sufficient potassium permanganate to form a dark pink solution.
2. Distill to dryness, collecting the distillate in a 500-ml glass screw-top bottle.
3. Store the sample in the capped glass bottle until ready for analysis.

4. Clean the electrolysis cells with distilled water, rinse with ethanol, and dry in a drying oven.

5. Pipet 50 ml of sample into a beaker. Add a few milliliters of this aliquot to the cool, dried electrolysis cell.

6. Add two pellets (~400 mg) of sodium hydroxide to the cell and dissolve.

7. Add the remaining portion of the 50-ml aliquot to the cell and stopper the cell.

8. Repeat steps 5-7 to the remaining samples and to one blank (dead water) and one low-level tritium standard (in the range of 50-100 pCi/liter).

9. Remove the stoppers from the cell, place the iron-nickel electrodes in the cells, place the glass tops on the cells pulling the electrode leads through the side arms.

10. Immediately place the cells in a pre-cooled constant temperature bath (5°-7° C) and connect the cells in series (red lead to black lead) with wire nuts.

11. Connect the free iron electrode lead of the cell at one end of the series to the positive lead of the constant current D.C. power supply and the nickel electrode lead at the other end of the series to the negative lead of the power supply.

12. Turn on the power supply and adjust the decade resistance box until the amperage of the power supply is 3 amps (24 ohms for 10 cells).

13. When the samples in the cells have decreased from 50 ml to the 25-ml line (24 hours), pipet 25 ml of blank, standard, and samples into the appropriate cells.

14. Repeat step 13 daily until eight 25-ml aliquots have been added.

15. When the last 25-ml aliquot has been added to the cells, permit the volume to decrease to the 25-ml line then decrease the resistance of the decade box until the power supply reads 0.3 amp.

16. Continue the electrolysis until the volume has decreased to or slightly below the 5-ml line on the cell. This step takes 8-9 days.

17. Turn off the power supply, disconnect the electrode leads, remove the cells from the constant temperature bath, remove the glass tops and electrodes from the cells and stopper the cells.

18. Place a small plug of glass wool in the glass ground joint adapter which connects the electrolysis cell with the vacuum trap.

19. Connect the cell, adapter, and tared vacuum trap to the vacuum system.

20. Immerse the vacuum trap in a Dewar of liquid nitrogen and apply vacuum.

21. Apply heat to the cell with a hot air gun to prevent ice formation and to increase the rate of distillation.

22. When a visual inspection indicates the water has been removed from the cell, discontinue heating. (The cell should be hot to the touch at this point.)

23. Continue the application of vacuum for 10-15 minutes. Feel the cell for cold areas which indicates the presence of water.

24. Turn off the vacuum, disconnect the apparatus, and remove the trap from the liquid nitrogen and cap the trap.

25. Allow the trap to reach room temperature.

26. Weigh the trap and record the weight of water collected.

27. Transfer the water from the trap to a tared liquid scintillation vial, weigh, and record the weight of water.

28. Proceed as in step 2 of "Determination of Tritium in Water," page 63.

CALCULATIONS

The weight of water removed from the cell in step 27 is used to obtain the enrichment factor (E.F.) from the enrichment chart.

The E.F. value and the tritium activity (pCi/liter) are used in the following formula to calculate the tritium concentration in the original sample in tritium units (T.U.).

$$\text{Tritium concentration (T.U.)} = \frac{A \times E.F.}{3.15}$$

where A = activity of enriched sample (pCi/liter)

E.F. = enrichment factor

3.15 = pCi/T.U.

The following equation is used to calculate error of the result.

$$2\sigma \text{ (T.U.)} = \frac{2\sqrt{\frac{G}{H} + \frac{B}{J}}}{2.22 \times 3.15 \times 0.005 \times E \times D}$$

where G = net sample cpm

B = background cpm

H = sample counting time

J = background counting time

2.22 = dpm/pCi

0.005 = sample volume counted, in liters

E = fractional counting efficiency

D = sample dilution factor (volume of sample divided by final volume counted, if a dilution to 5 ml is necessary)

ELECTROLYSIS CELL

This cell was developed at the University of Miami by Dr. Gote Ostlund for the electrolytic enrichment of tritium in alkaline solution. The cell is also used for the final distillation of the enriched sample.

For distillation, an adapter and receiver are substituted for the funnel top.

The cells are available in lots of 10 from

Science Glass
2245 S.W. 28th Street
Miami, Florida 33133

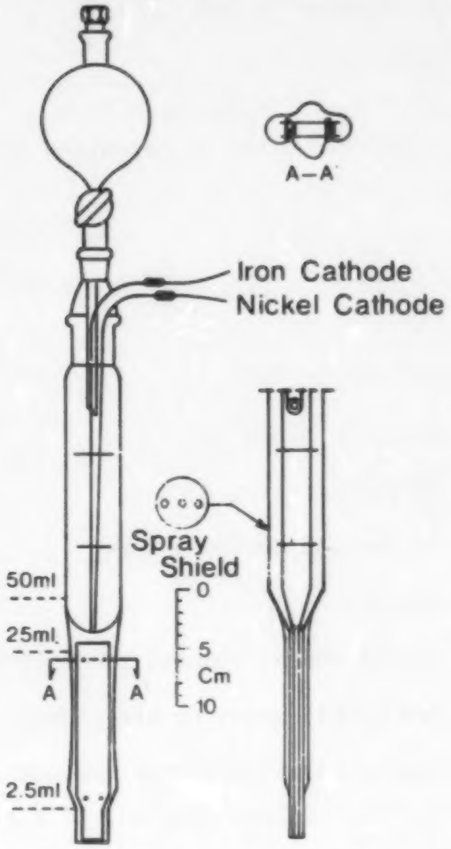

A—A
Iron Cathode
Nickel Cathode
Spray Shield
50ml
25ml
A
A
0
5
Cm
10
2.5ml

Figure 10. Alkaline Electrolysis Cell

THE COLLECTION AND DETERMINATION OF TRITIUM IN THE ATMOSPHERE

PRINCIPLE OF THE METHOD

This method describes a routine method for the collection and determination of tritium as hydrogen and as moisture in the atmosphere. The atmospheric sample is passed through a molecular sieve trap to remove the moisture. Tritium-free hydrogen is added as a carrier. The carrier hydrogen and atmospheric hydrogen are converted to water using a palladium black catalyst. This water is collected in a second molecular sieve trap. The water collected on these two traps is removed by heating, and is subsequently analyzed for tritium.

REAGENTS

Electrolyte
Palladium catalyst
Tritium-free water

APPARATUS

The total sample consists of two parts: one, a "field box" (Figure 11) and two, a permanently-located field station (Figure 12). The laboratory portion consists of a multiple distilling apparatus for the recovery of the water. The "FIELD BOX" is a foam-filled wooden box with cutouts for

Molecular sieve trap M1, 400 grams of molecular sieve 4A
Molecular sieve trap M2, 250 grams of molecular sieve 4A

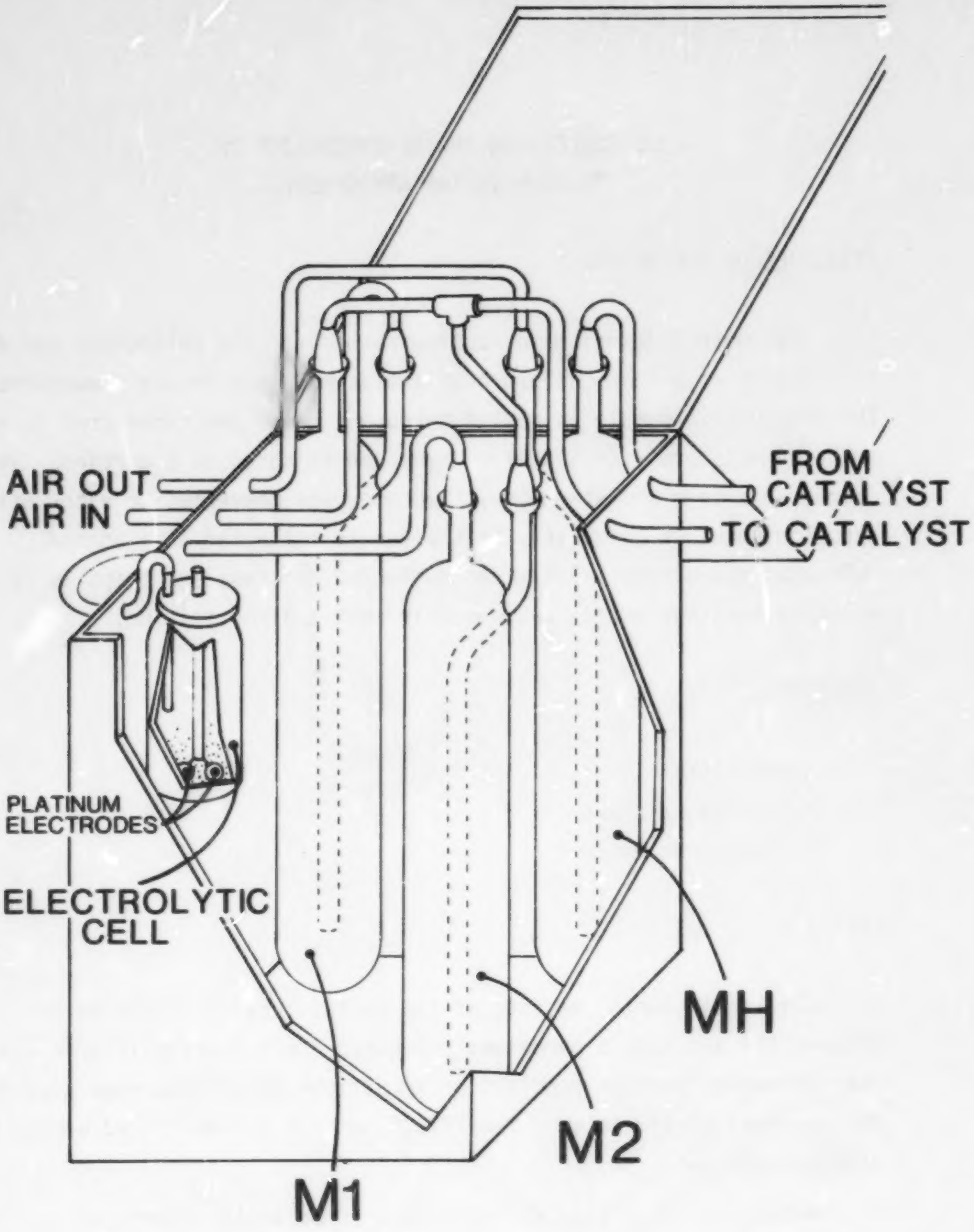

AIR OUT
AIR IN
FROM CATALYST
TO CATALYST
PLATINUM ELECTRODES
ELECTROLYTIC CELL
MH
M2
M1

Figure 11. Hydrogen in Air, Field Box

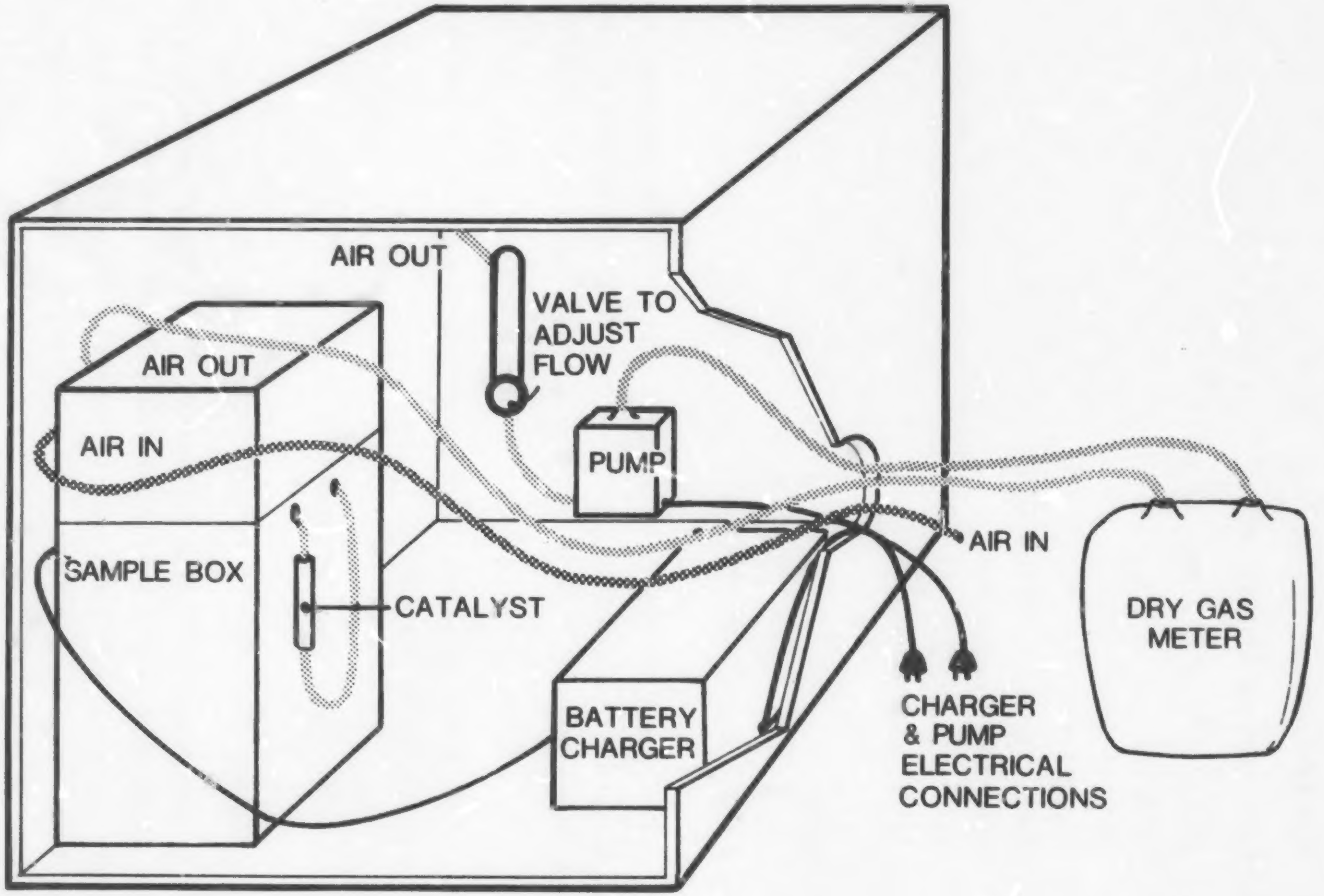

AIR OUT
VALVE TO ADJUST FLOW
AIR OUT
AIR IN
PUMP
SAMPLE BOX
CATALYST
BATTERY CHARGER
AIR IN
CHARGER & PUMP ELECTRICAL CONNECTIONS
DRY GAS METER

Figure 12. Hydrogen in Air, Field Station

Molecular sieve trap MH, 250 grams of molecular sieve 4A
Electrolytic cell

The field station consists of:

Battery charger, 1 amp, 12 volts
Catalyst
Dry gas meter
Flowmeter
Pump, fish tank, Silent Giant
Recording thermometer
Refrigerator, 2.1 ft^3
Valve, needle

PROCEDURE

A. Preparation of the Field Box

1. Label glass traps with the sample station number and use, i.e., M1, M2, and MH. Record the weight of the traps containing the dry molecular sieves and the other pertinent data on the work sheet.

2. Fill electrolytic cell with 70-ml electrolyte, weigh, and record.

3. Place traps and electrolytic cell into the field box and make all connections as illustrated in Figure 11.

B. Sampler Preparation in the Field

4. Connect field box to system (Figure 11).

5. Turn on pump and check for leaks. This is accomplished by pinching intake hose and observing the float in the flowmeter. Float should return to zero. All leaks must be corrected before proceeding. Record gas meter reading, air flow rate, date and hour, sampler number, and station on sample card.

6. Remove clamp from electrolytic cell.

7. Install a new chart in the recording thermometer.

C. Sampler Removal

8. Check for leaks as before and note if any developed.

9. Record flow, gas meter reading, date and time on the sample card. Remove temperature chart and return it with the sampler and sample card.

D. Laboratory Disassembly

10. Remove and weigh the electrolytic cell and glass traps. Record on work sheet.

E. Water Recovery for Traps M1 or MH

11. Place in the multiple distillation unit. Adjust heat to obtain 350° [illegible] in 30 minutes. Using helium as a carrier, distill the water into a trap cooled with liquid nitrogen. All of the water should distill over in 1 hour. If volume of water is less then 9 ml, add appropriate volume of distilled well water to make volume approximately 9 ml.

12. After all of the water is distilled over into the traps, turn off the helium and vacuum and remove the trap from LN immediately. Allow trap to come to room temperature. Record weight in appropriate column on work sheet. Save the water for tritium analysis as in "Determination of Tritium in Water," page 63.

13. De-gas M2 as in steps 11 and 12 for reuse. Do not save this water.

CALCULATIONS

$$V_o\ (m^3) = V_1 \times \frac{P_1}{760} \times \frac{273}{273 + T_1}$$

where V_o = volume of sample collected at STP

V_1 = volume in cubic meters = dry gas meter volume in cubic feet × meter calibration factor × $0.0283 m^3/ft^3$

T_1 = median temperature on recording chart (°C)

P_1 = barometric pressure in mm Hg for station elevation, assuming pressure at sea level is 760 mm Hg

$$\text{Hydrogen efficiency} = \frac{\text{weight water on MH trap}}{\text{weight water loss from electrolytic cell} - \text{weight water on M2 trap}}$$

$$\text{HTO}\ (pCi/m^3) = \frac{A_{mi} \times V_{mi}}{V_o}$$

$$\text{HT}\ (pCi/m^3) = \frac{A_{mh}\ V_{mh}}{V_o \times H_2\ \text{efficiency}}$$

$$\text{Tritium}\ (pCi/ml) = A_{mi}$$

where A_{mi} = pCi/ml of water recovered from M1 trap

V_{mi} = volume of water recovered from M1 trap

A_{mh} = pCi/ml of water recovered from MH trap

V_{mh} = volume of water recovered from MH trap (plus any added water to make $V_{mh} > 9$ ml)

THE ANALYSIS OF FOOD AND MILK FOR CARBON-14

PRINCIPLE OF THE METHOD

This method describes a procedure for the determination of carbon-14 in various biological materials. The dried sample is combusted in a Parr bomb and the products of combustion, carbon dioxide and water, are separated and collected. The carbon dioxide is converted to benzene by the following reactions:

$$2CO_2 + 10Li \xrightarrow{500^\circ\ C} Li_2C_2 + 4Li_2O$$

$$Li_2C_2 + 2H_2O \longrightarrow C_2H_2 + 2LiOH$$

$$3C_2H_2 \xrightarrow{cat} C_6H_6$$

The benzene formed is analyzed for carbon-14 by liquid scintillation spectroscopy.

REAGENTS

Durabead #1 catalist - Mobile Chemical Company
Liquid scintillation cocktail
Lithium metal, stored under argon
Oxygen, radon-free
Sulfuric acid: 20%

APPARATUS

Gas handling system as illustrated in Figure 13

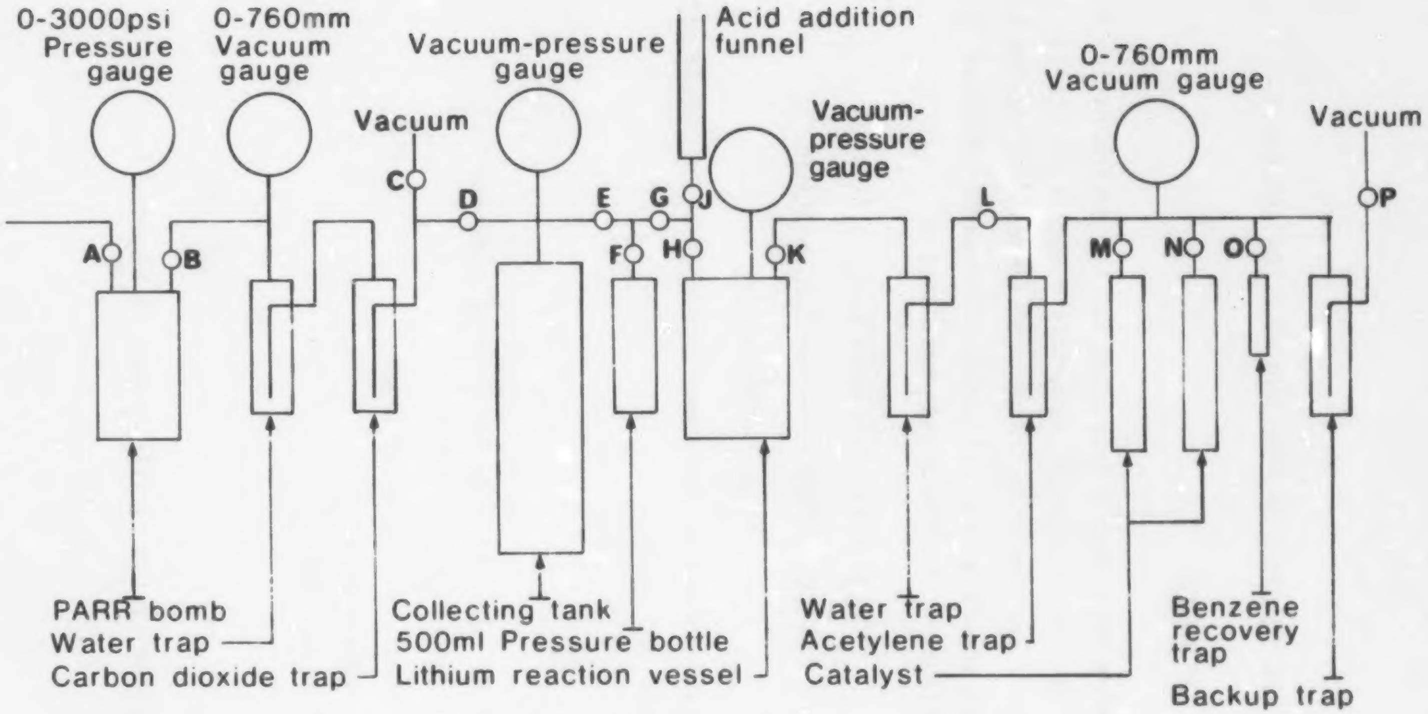

0-3000psi Pressure gauge
0-760mm Vacuum gauge
Vacuum
Vacuum-pressure gauge
Acid addition funnel
Vacuum-pressure gauge
0-760mm Vacuum gauge
Vacuum
A
B
C
D
E
F
G
H
J
K
L
M
N
O
P
PARR bomb
Water trap
Carbon dioxide trap
Collecting tank
500ml Pressure bottle
Lithium reaction vessel
Water trap
Acetylene trap
Catalyst
Benzene recovery trap
Backup trap

Figure 13. Benzene Synthesis Apparatus

PROCEDURE

1. Prepare 200 grams of wet sample dried at room temperature and a vacuum of 1 mm of mercury. Weigh 15 grams of the dried sample into a nickel combustion capsule. Add two drops of distilled water and compress to form a hard pellet.

2. Place the bomb head in the tripod support ring and adjust the capsule so that the top of the cup is 6 to 7 inches from the underside of the bomb head. Fasten a 10-cm length of ignition wire to the electrode hooks and bend the wire so that it touches the sample but not the capsule. Use a volt-ohm meter to check for continuity.

3. Check the gasket to be sure it is in good condition, then push the bomb head firmly in the cylinder. Slide the two-ring section into position and raise the band from the bottom of the bomb to encircle the ring section. Adjust band so that its cone-pointed screw enters the slot between the ring section, then tighten the six screws to lock the closure. A light pull on the wrench will be sufficient to tighten these screws.

4. Place the bomb in the barricade and bucket. Fill the bucket with cold water. Connect the oxygen hose inlet to the special filling inlet valve, and the discharge valve (B) to the vacuum line (Figure 13). Check for leaks by opening the vacuum valve (C) and evacuating the bomb. Pressure should drop to 100-200 microns and hold when vacuum valve (C) is closed. Correct any leaks before proceeding.

5. After checking for leaks, open the oxygen valve (A) very slowly and admit oxygen to not more than 325 psi at room temperature.

6. Connect the ignition unit to the terminals on the bomb head and fire, making sure all safety precautions are observed. After firing, the pressure will increase rapidly during the first 3 to 5 seconds. The pressure in the bomb will return to approximately 325 psi when the combustion is complete. Disconnect ignition unit. Allow the bomb to cool before making any withdrawals.

An occasional sample will appear to explode (an extremely high pressure will be noted). This is caused by:

(1) too rapid an addition of oxygen
(the flour dust explosion)

(2) insufficient water in sample

(3) insufficient pelletizing, or

(4) lack of good judgment.

7. With the bomb cool and connected to the water trap in dry ice acetone (DIA) and carbon dioxide trap in liquid nitrogen (LN) and the vacuum valve (C) closed, slowly open the bomb discharge valve (B) and allow the gases to escape into the traps. Water will be trapped in the DIA trap, carbon dioxide, (CO_2), and oxygen will condense in the LN trap. Do not exceed 300 mm of mercury on the vacuum gauge. After all the gases have been transferred, close valve to water trap and open the vacuum valve and pump on the carbon dioxide until the system pressure is below 1 mm of mercury pressure.

8. Valve (E) must be closed. Close the vacuum valve (C) and open valve (D). Remove LN from the frozen carbon dioxide trap and allow the carbon dioxide to expand into the collecting tank. Record final pressure reading and temperature. (Volume of tank must be known.)

9. Transfer the carbon dioxide to a 500-ml stainless steel bottle by placing the evacuated bottle in LN and condensing the carbon dioxide from the collecting tank.

10. The lithium reaction vessel (Figure 13) must be thoroughly dry. Connect the tap water to the lower jacket inlet and a waste line to the water outlet. Adjust the water flow to give a good flow of water through the cooling jacket.

11. Transfer lithium metal into the reaction vessel through the removable quartz window. Use 10-20% excess lithium metal. (1.7 g of lithium per liter of Co_2 represents an approximate 10% excess.) Eight

pieces of 12-mm lithium rod, three inches long, have been found to be sufficient for the 15-gram sample.

12. With the lithium metal in the reaction vessel and the window replaced, place the vessel into the crucible furnace and evacuate. A leak at this point can be observed on the system vacuum gauge. Set the furnace at 600° C and turn on. The pressure on the system will gradually increase (de-gassing of the lithium) but at a temperature of approximately 180° C the lithium will be molten and the vacuum pressure should decrease to 10^{-3} mm of mercury or less. When the temperature of the lithium reaches 400° C, cut off the vacuum source and slowly add the carbon dioxide to the lithium. Allow the pressure on the pot vacuum gauge to increase to about 125 mm of Hg. A dull red glow can be seen through the quartz window. A green glow indicates the presence of oxygen (the source of oxygen must be sought and eliminated). Keep the pressure at 125 to 175 mm of mercury until the control valve of the 500-ml stainless steel bottle is full open.

13. As soon as the sample bottle valve is open, increase the temperature of the furnace to 900° C and leave there for one hour. Turn off furnace, close all valves, remove lithium pot, and allow to cool to room temperature before proceeding.

14. Activate the two catalytic tubes by heating to 350° C for 3 hours and at a vacuum of <0.1 mm of Hg, collecting any water in the backup trap, then close the valves to these tubes (valves M, N).

15. Connect the outlet of the lithium pot to the glass sytem and a 250-ml separating funnel to the inlet. Water should still be circulating through the water jacket.

16. Open valves K, L, and P, to a good vacuum source. (PUMP MUST BE VENTED TO THE OUTSIDE, AS HYDROGEN GAS IS EVOLVED.) When a vacuum of <0.1 mm of mercury is obtained, close valve P. The water trap (T_2) should be at DIA temperature and the acetylene and backup traps at LN temperature. Carefully add 250 ml distilled water. Do not allow the

pressure on the system to go over 300 mm of Hg. Adjust the stopcock on the separating funnel and valve P to accomplish this.

17. Follow the first 250 ml of water with 500 ml of 20% sulfuric acid solution and then by 1500 ml of water. The large volume of liquid will react with any lithium, lithium carbide, or lithium oxide that has splattered on the walls of the reaction vessel.

18. After the water has been added to the reaction vessel, allow the system to pump down slowly to out-gas the vessel. Then close the outlet valve (K) and continue to pump down the glass vacuum system for 15 minutes to remove the last traces of hydrogen.

19. Close valves L and P to isolate the acetylene, and open the two valves (M and N) to the catalytic tubes. Remove the LN from the backup trap and allow the acetylene to expand back into the acetylene trap or catalytic trap. Remove the LN from the acetylene trap and replace with an empty, cold (-195° C) trap. This will allow the acetylene to expand at a low steady rate and not overheat the catalyst. This reaction is best done overnight as 8 to 10 hours is required.

20. To recover the benzene, cool the backup trap with DIA and heat the catalyst tubes to 150° C. Remove unreacted acetylene by vacuum pump. Vacuum distill the benzene to a removable cold trap cooled with LN. Close off the catalyst tube and the vacuum pump from this system for the final transfer. Transfer the benzene to a weighed scintillation counting vial and determine the weight of recovered benzene.

21. To the weighed benzene in a scintillation counting vial, add 4.0 ml of the liquid scintillation solution.

22. Prepare a background sample by adding 4.0 ml of the scintillation solution to the same weight of spectrographic-grade benzene. Store the vials in the dark overnight and count for two 100-minute intervals in the proper carbon-14 window.

23. To determine individual counting efficiencies, add 0.10 ml of a standard carbon-14 solution approximately 1.0×10^6 cpm/ml to the sample and background sample.

CALCULATIONS

$$\text{Carbon-14 (dpm/g carbon)} = \frac{A \times \text{cpm}}{\text{eff} \times B}$$

where A = fraction of carbon in benzene

cpm = gross counts - background

$$\text{eff} = \frac{\text{cpm (internal standard)}}{\text{dpm (internal standard)}}$$

B = grams of benzene counted

ANALYSIS OF URANIUM BY FLUOROMETRY

PRINCIPLE OF THE METHOD

This procedure describes a method for the determination of uranium in environmental samples. After dissolution of the sample, a uranium-uranium fluoride complex is formed that will fluoresce under ultraviolet light, unlike the contaminants. This method combines the advantages of several existing methods to reduce "inherent errors," operation error, and procedural tedium.

REAGENTS

Aluminum nitrate
Ammonium hydroxide: concentrated
Hydrofluoric acid: concentrated
Iron carrier
Methyl isobutyl ketone
Nitric acid: concentrated; 4N, 50%
Perchloric acid
Potassium pyrosulfate: crystals
Sodium-potassium flux
Sulfuric acid: concentrated

APPARATUS

Platinum dish, 50-ml
Platinum dish, pellet-size
Propane torch
Turner Fluorometer (Note a for operating instructions)

PREPARATION OF SAMPLE

A. Soil and Sediments

Total dissolution of sample is sometimes a rather difficult and lengthy process but analogous to the procedure for dissolution of thorium sediments given elsewhere in this manual. After dissolution, continue at C, 2, step a.

B. Air Filters

Depending on the residue on the filter, the sample may subsequently need treatment as a sediment sample with extraction of uranium. At first, depending on filter type, the sample is treated as follows:

1. Nylon Mesh Membrane

a. Fold the filter into a 250-ml beaker and add 30 ml concentrated nitric acid plus 5 ml sulfuric acid.

b. Digest on a hot plate, slowly evaporating the nitric acid.

c. Allow the remaining sulfuric acid to char some of the organic material, then cautiously add more concentrated nitric acid until brown fumes have vanished.

d. Repeat steps b and c until no more charring occurs and no more nitric acid decomposes.

e. Transfer the material to a small platinum dish (50-ml). Evaporate to fumes of sulfuric acid, and then to dryness. If the amount of residue is very small, proceed. Otherwise, treat sample as soil or sediment. (Iron carrier may have to be added.)

f. Add 5 ml concentrated hydrofluoric acid and 2 ml perchloric acid cautiously and evaporate to dryness.

g. Evaporate to dryness twice in the presence of 2 ml concentrated nitric acid.

h. Add 20 ml 4N nitric acid, warm to dissolve, and transfer to a 50-ml volumetric flask with 4N nitric acid. Continue at C.

i. If insoluble residue remains after step h, a pyrosulfate fusion may be necessary followed by hydroxide precipitation. See soil and sediment dissolution procedure.

2. Membrane Filters without Nylon

a. Digest the filter for a short time with a mixture of 5:1 nitric-perchloric acid in a covered Teflon beaker. Work in a perchloric acid hood.

b. Evaporate until about one-third or original volume of perchloric acid remains.

c. Add 5 ml concentrated hydrofluoric acid to the perchloric acid mixture and evaporate to fumes of perchloric acid and then to dryness.

d. Add 20 ml 4N nitric acid and warm to dissolve. Transfer to a volumetric flask with 4N nitric acid and dilute to volume with 4N nitric acid. Continue at C, 2, step a.

C. Water

Initially, an incoming water sample can be filtered and a 0.25-ml aliquot taken, evaporated into a platinum dish, and analyzed directly for uranium. If the first fluorometric analysis indicates too large a suppression of fluorescence, treat the sample as an effluent.

1. Total Sample Analysis

Shake sample thoroughly and remove a 10-ml aliquot. Centrifuge or filter and run two separate analyses for water and sediments, or evaporate the aliquot to dryness and treat as a sediment. If the amount of sediment is small, the treatment described for membrane filters without nylon might do.

2. Effluents (High in Dissolved Solids)

The following procedure eliminates most interference with exception of large quantities of iron with chloride and perhaps sulfate and chlorate which carry over into the organic fraction. Try total sample analysis if high suppression is encountered after extraction. (Anion interference may be removed by precipitation of uranium on 1 to 2 mg ferric ion from about 30 ml at pH 9.)

a. Pipet a 20-ml aliquot to a 50-ml screw-cap ketone-resistant plastic centrifuge tube.

b. Add 0.5 ml concentrated nitric acid if sample is not made up in 4N nitric acid.

c. Add 20 ml aluminum nitrate salting solution to tube and mix well immediately.

d. Add 10 ml methyl isobutyl ketone accurately with pipet.

e. Cap tube firmly but not too tight. Check for leaks.

f. Shake tube for 3 minutes.

g. Centrifuge 5 minutes to separate phases cleanly.

h. Pipet a 100 λ to 250 λ aliquot from the upper ketone layer into the small platinum fluorometry dish and evaporate to dryness gently under an infrared lamp. Gently flame the dish until the organic residue has disappeared.

PROCEDURE

1. Mount a propane torch so that the flame will project straight up. Ignite torch and allow to burn at low flame until valve region becomes warm whereupon a less variable, more controllable small flame will be had.

2. Mount an adjustable guide, such as a ring, about 5 cm above the torch as a rest for the platinum or nichrome heavy-gauge wire dish holder.

3. Place the platinum dish in the wire holder and scoop in an overflowing amount of flux. Level off the excess.

4. Fuse over a low flame, adjusting the height of the ring so that complete fusion takes place in about 30-45 seconds.

5. Allow melt to partially solidify and reheat, swirling gently as last particles liquify. Circle edge of dish over flame. Avoid heating to visible redness in ordinary room light.

6. Remove dish from flame and allow to solidify completely. Allow to cool for a few minutes (store in dessicator if necessary).

7. Establish background fluorescence of pellet (F_B) as in Note a. Handle pellet with tweezers and avoid chipping.

8. Return the pellet to the dish containing the dried sample aliquot, and establish the new fluorescence (F_2) after repeating steps 4 through 6.

9. Rinse the dish in 50% nitric acid and water and dry it.

10. Pipet in 0.1 ml uranium standard and evaporate. Two uranium standards are prepared (4.00 and 0.400 g/liter). Generally select that amount whose fluorescence is greater than that appearing for the sample.

11. Return the pellet to the dish and obtain a third fluorescence (F_3) as in steps 3 through 6.

12. Clean the dish by dipping in fused potassium pyrosulfate and digesting for 30 minutes in 1:1 hot nitric acid.

13. With each series of samples run at least three standards pellets, that is, establish three successive fluorescence values (one background plus two successive standard additions) for three different pellets. (Note b)

14. Consider the data obtained thus far:

If $F_2 < F_B$ treat sample as an effluent and repeat analysis. The terms "quenching" or "suppression" refer to the ability of foreign substances to inhibit uranium fluorescence. In a few cases where the sample fluorescence approaches the magnitude of the background, and high quenching effects are taking place, consideration of background quenching might have to be made to avoid low results.

(a) Extract sample to remove interference; or,

(b) Correct the background for quenching. (See ALTERNATE METHOD.)

CALCULATIONS

The procedure just described obviates consideration of pellet weight variation as well as presence of small amounts of uranium fluorescence inhibitors. These effects are also operative on the internal standard added to the sample and the net effects cancel out.

1. $$\text{Uranium } (\mu g/\text{pellet}) = \frac{F_2 - F_B}{F_3 - F_2} \times \text{g uranium standard}$$

$$\text{Uranium } (\mu g/\text{sample}) = \text{g/pellet} \times \text{dilution or aliquot}$$

2. Empirical Correction Factor

For each of the standards calculate ΔF where

$$\Delta F = \frac{F_3 - F_2}{F_2 - F_B}$$

Then find the average ($\overline{\Delta F}$) for the set of standards (Note c).

3. Multiply the result found in 1 by $\overline{\Delta F}$ whenever $\overline{\Delta F}$ differs significantly from 1.00.

$$\text{Uranium, corrected } (\mu g/\text{sample}) = \mu g/\text{sample} \times \overline{\Delta F}$$

ALTERNATE METHOD

This method overcomes the problem of re-heating the pellet for the third time as well as patience required to prepare pellets of identical weight. Pellet weight variations may be rather large, an internal standard need not be determined, and a ΔF factor need not be calculated. This method attempts to simplify analysis of a large number of samples with the restriction that quenching is not accounted for. (It is useful for fresh water samples and many samples extracted by methyl isobutyl ketone.)

At least one series of determinations should be made using the internal standard; the net fluorescences of standards alone are plotted against pellet weight in milligrams on linear graph paper. The best straight line is drawn through the points. Use the points lying nearest the line for the following:

> Select the sample having the lowest weight as the "normal pellet." Determine the correction factor necessary to raise the observed fluorescence of the remaining standards to the fluorescence of the "normal pellet" and plot this factor against the respective pellet weight on two-cycle semi-log paper. The resulting line is used to normalize future F readings (background subtracted) to a common pellet weight. At least three standard pellets should be run identically with each set of unknowns and averaged.

CALCULATIONS

Normalize $(F_2 - F_B)$ to F^*

$$\text{Uranium } (\mu g/\text{sample}) = \frac{F^* \text{ sample}}{F^* \text{ standard}} \times \mu g \text{ uranium standard} \times \text{dilution factor}$$

where F^* = normalized value

SUPPLEMENTARY CALCULATIONS

To correct for background quenching, it is necessary to determine a suppression factor:

For the three standards run with the unknowns, normalize the value $F_2 - F_B$ above to obtain F* for the standard. Then find the average ($\bar{F}$* standard) and divide it by μg uranium in the standard.

Similarly, for the sample find the value $1/\Delta F$ $(F_3 - F_2)$ and normalize it to obtain F* for the sample standard. Divide this by μg uranium added to the sample. The quenching factor is then F*ss/μg uranium added divided by $\bar{F}$ standard/μg uranium standard.

Notes: a. Operation of the Instrument - Turner Model 110:

1. Turn on the unit (activate mercury lamp by forcing slightly full clockwise and release) with the pellet holder door open and allow to warm up for one hour. (Filter 2A-12 on left side; filter 7-60 on right side.)
2. Set the meter to zero with the zero control.
3. Close the door after having blocked the pellet aperture with some opaque substance (electrical tape).
4. Set dial so that scale divisions equal zero, and re-zero the meter using the blank knob.
5. Repeat steps 2, 3, and 4 at least once for several positions of the meter sensitivity control to obtain meter behavior which is neither too sluggish nor erratic.
6. Open door, remove tape, and place a background pellet in the sample holder.
7. Close door and rotate fluorescence dial until meter is zeroed. If this is not possible, or if the reading is less than 10, adjust the range selector so that the background falls

at about 60 scale divisions or less. The range selector is left permanently in this position (or until a new batch of flux produces pellets giving a significantly different background).

8. Replace background pellet with sample or standard pellet and read the fluorescence at meter zero point. If the needle is off scale to the left, indicating higher concentrations, place at $10^{1.0}$ neutral density filter over the yellow filter. If more than $10^{3.0}$ density is required, dilute the sample and repeat analysis.

9. When running a series of pellets, recheck zero setting and blank knob after several determinations.

b. If erratic results are gradually obtained on replicate samples, the flux should be suspected as "aging" and a new batch prepared.

c. This factor ($\overline{\Delta F}$) has been found to vary with the age of the flux and its initial value seems to depend on the heating the flux receives when first prepared.

RADIOCHEMICAL DETERMINATION OF THORIUM IN ENVIRONMENTAL SAMPLES

PRINCIPLE OF THE METHOD

The sample is solubilized with nitric acid following appropriate concentration and decomposition pre-treatments. Thorium is separated from calcium and sodium by co-precipitation with ferric hydroxide to prevent precipitation of calcium fluoride and sodium aluminum fluoride. Separation from iron, titanium, and zirconium is accomplished by co-precipitation with lanthanum or yttrium fluoride. The thorium is separated from the lanthanum or yttrium for counting or electrodeposition by solvent extraction of the thenoyltrifluoroacetone complex.

REAGENTS

Ammonium hydroxide: concentrated, 50%, 20%
Hydrochloric acid: concentrated
Hydrofluoric acid: 48%
Hydrogen peroxide: 30%
Iron carrier: 10 mg iron/ml, 1 mg/iron/ml
Lanthanum carrier: 10 mg lanthanum/ml
Nitric acid: concentrated, 2N. 0.2N, 50%
Thenoyltrifluoroacetone (TTA): 10% in xylene
Thymol blue: 0.1%
Wash solution (6% nitric acid, 3% hydorfluoric acid)
Yttrium carrier (purified): 15 mg yttrium/ml

APPARATUS

Beaker, Teflon
Burner, Mahar
Centrifuge
Mixer, Vortex

PREPARATION OF SAMPLE

A. Water Samples

1. Filter through a 0.45-μ membrane filter and stabilize the filtrate by acidifying to 2% with concentrated hydrochloric acid. Note volume filtered and reserve suspended solids for separate analysis.

2. Transfer one liter of filtered water to a one-liter beaker. Add 20 ml of concentrated nitric acid, 10 ml of 10-mg iron per ml carrier solution and 3 ml of 10-mg lanthanum per ml carrier solution. Evaporate to dryness on a steam bath or hot plate.

3. Add 10 ml of concentrated nitric acid and 100 ml of water. Cover and heat until the residue has dissolved. Proceed with the hydroxide separation.

B. Sediment and Soil Samples

1. Weigh 1 gram of sample, dried and ground to pass a 100 mesh sieve, into a porcelain crucible and ash overnight at 550° C.

2. Transfer sample to a 100-ml Teflon beaker and evaporate twice to dryness with 10-ml portions of concentrated hydrochloric acid.

3. Dry in oven at 100° C for 2 hours or overnight to dehydrate silica.

4. Add 2 ml concentrated hydrochloric acid and 20 ml of water and heat while covered for 30 minutes. Decant liquid into a 40-ml centrifuge tube. Centrifuge at 2000 rpm for 5 to 10 minutes. Decant supernatant liquid into a 250-ml centrifuge bottle and transfer the residue to the Teflon beaker.

5. Add 15 ml of 48% hydrofluoric acid and 10 ml of concentrated hydrochloric acid to the residue and evaporate to dryness on a hot plate. Remove fluoride by three successive evaporations to dryness with 5-ml portions of 6N hydrochloric acid.

6. Add 2 ml of concentrated hydrochloric acid and 20 ml of water. Cover and heat for 30 minutes and then transfer to the same 50-ml centrifuge tube used in step 4. Centrifuge and decant supernatant liquid into the centrifuge bottle containing the first dissolved portion. Transfer the remaining residue to a 50-ml platinum dish, add 5 ml of concentrated hydrochloric acid and 5 ml of 48% hydrodluoric acid and evaporate to dryness.

7. Add one gram of potassium pyrosulfate to the platinum dish and fuse over a Mahar burner. Cool, add 2 ml of concentrated hydrochloric acid and 20 ml of water, and heat until residue has dissolved. Combine with the other dissolved portions in the 250-ml centrifuge bottle.

8. Add one ml of 10 mg/ml iron carrier per gram of sample. If less than one gram of sample was taken, add an additional one ml of iron carrier for each 100 mg of weight below 1 gram. Proceed with the hydroxide separation of thorium.

C. Air-Borne Dust and Suspended Solids Collected on Membrane Filters

1. If the solids weigh from 0.1 to 1 gram, ignite in a porcelain crucible or dish and proceed as for sediment and soil samples. If the weight is less, wet ash the filter in a covered 150-ml borosilicate beaker with repeated additions of concentrated nitric acid in the presence of 1 ml of concentrated sulfuric acid.

2. Transfer solution and residue to a 50-ml platinum dish, add 5 ml of 48% hydrofluoric acid, evaporate until the fumes of sulfuric acid are given off, add 1 gram of potassium pyrosulfate, heat to volatilize sulfuric acid and fuse the pyrosulfate. Dissolve the residue in 3 ml of concentrated nitric acid and 20 ml of water, transfer to a 250-ml centrifuge bottle, add 10 ml of 10 mg/ml iron carrier and proceed with the hydroxide separation of thorium.

PROCEDURE

A. Hydroxide Separation of Thorium

1. Transfer sample to a 250-ml centrifuge bottle and, while swirling, add concentrated ammonium hydroxide from a burette to incipient precipitation of the iron (permanent amber color). Increase the volume to about 190 ml by adding distilled water and then add 15 ml of concentrated ammonium hydroxide slowly while mixing. Allow to stand one hour and centrifuge at 1800 rpm. Decant and discard the supernatant liquid.

2. Add 10 ml of concentrated nitric acid to the beaker which had contained the sample. Cover, and heat on a hot plate until the acid refluxes to the top of the beaker. Cool and wash down the sides of the beaker with about 10 ml of water.

3. Pour the diluted acid from the beaker into the centrifuge bottle in such a way as to wash down the sides of the bottle and transfer the remaining acid from the beaker to the bottle with several water washes. Swirl the centrifuge bottle to dissolve the precipitate and dilute to about 100 ml.

4. Add concentrated ammonium hydroxide from a burette to incipient precipitation, dilute to about 190 ml, and add 10 ml of concentrated ammonium hydroxide slowly with mixing. Allow to stand one hour and centrifuge at 1800 rpm. Decant and discard the supernatant liquid.

5. Slurry the precipitate by striking the bottle against the heel of the hand and then add water to 200 ml. Centrifuge at 1800 rpm. Decant and discard the wash.

6. Using a pipet, add 3 ml of concentrated nitric acid to the centrifuge bottle in such a way that the precipitate adhering to the sides will dissolve. Swirl the bottle to dissolve the precipitate. If the precipitate fails to dissolve completely, add 10 drops 30% hydrogen peroxide.

B. Fluoride Separation of Thorium

1. Transfer the solution and any precipitate of silica from the centrifuge bottle to a 50-ml polypropylene centrifuge tube with distilled water and dilute to about 30 ml. If lanthanum or yttrium carrier was not previously added, add at this point and mix.

2. Add 5 ml of 48% hydrofluoric acid, mix, and allow to stand for one hour.

3. Centrifuge at 1600 rpm for 5 minutes. Decant and discard the supernatant liquid.

4. Disperse the precipitate with the Vortex mixer in 5 to 10 ml of a wash solution containing 6% nitric acid and 3% hydrofluoric acid, and centrifuge at 1600 rpm. Decant and discard the wash solution.

5. Repeat step 4.

6. Add 5 ml of concentrated nitric acid to the precipitate, disperse with the Vortex mixer and pour into a 30-ml Teflon beaker. Repeat with a second 5-ml portion of nitric acid and then with two 5-ml portions of water. Add 1 ml of 70% perchloric acid and, in a perchloric acid hood, evaporate on a hot plate overnight. The residue generally will not go completely to dryness.

7. Add 2 ml of concentrated nitric acid and evaporate nitric acid on a hot plate. Repeat with 2 ml more of nitric acid.

8. Add 5 ml of 2N nitric acid, cover, and heat for 10 minutes to dissolve the residue.

C. Extraction of Thorium with Thenoyltrifluoroacetone (TTA)

1. Add the amount of freshly prepared ascorbic acid solution which will decolorize 5 mg of iron and then add one drop of 0.1% thymol blue. Adjust to pH 2.0 (salmon pink color) with 50% ammonium hydroxide and 2N nitric acid. Make the final adjustment with 0.5N ammonium hydroxide and 0.5N nitric acid.

2. Transfer the sample to a 125-ml separatory funnel with a wash solution at pH 1.5 (adjust 0.1N nitric acid to pH 1.5 with ammonium hydroxide using a pH meter). Use enough wash solution to end up with 15 ml total volume.

3. Add 15 ml of 10% TTA in xylene and shake for 15 minutes. Drain off and discard the aqueous layer.

4. Add 5 ml of 0.2N nitric acid to the organic layer and shake for five minutes. Drain off and discard the aqueous layer. Repeat this wash step with two additional 5-ml portions of 0.2N nitric acid.

5. Add 15 ml of 2N nitric acid to the organic layer and shake for 15 minutes to strip the thorium from the organic layer. Drain the aqueous layer into a 30-ml borosilicate beaker. Repeat the stripping with a second 15-ml portion of 2N nitric acid.

6. Add 1 ml of 70% perchloric acid to the beaker and, in a perchloric acid hood, evaporate to dryness on a hot plate.

D. Mounting of Thorium for Alpha Counting

1. Add 2 ml of concentrated nitric acid to the beaker. Cover, and digest for 20 minutes.

2. Add 1 ml of iron carrier (1 mg iron/ml) to the 30-ml Teflon beaker retained above. Transfer the solution from step 1 into the Teflon beaker and adjust the volume to 15 ml.

3. Add 10 ml of 50% ammonium hydroxide slowly by burette while stirring. Cover and let stand for one hour.

4. Prepare a planchet by cleaning in 50% nitric acid and drying. Add about 14 drops of adhesive solution to planchet and spread over entire surface. Let stand until the solvent has evaporated.

5. Stir and filter the solution in the beaker on a membrane filter apparatus using a 0.45-micron, 47-mm membrane filter. (Wet filter prior to filtering sample.) Wash beaker and filter funnel with 5% ammonium hydroxide.

6. Remove funnel top. Carefully place membrane filter on planchet. Use stirring rod to press around outside edge to seal filter to planchet. Place planchet in drying oven at 80°-105° C for at least two hours prior to counting. If possible, dry overnight.

CALCULATIONS

$$\text{Thorium-230 (pCi/liter)} = \frac{R_s - R_{bkg} - C}{A \times B \times D}$$

where R_s = alpha count rate of sample (c/m)

R_{bkg} = alpha counter background (c/m)

C = sample blank (pCi) calculated by using equation for pCi thorium/sample

A = calibration factor obtained by counting a known amount of thorium-230 mounted as described above

B = yield

D = sample volume in liters

ION EXCHANGE SEPARATION OF PLUTONIUM

PRINCIPLE OF THE METHOD

The following procedure applies to a prepared solution of a sample in 30 to 60 ml of 6N hydrochloric acid. The solution is adjusted to 9N hydrochloric acid concentration. The plutonium is stabilized in the +4 valency state with hydrogen peroxide and adsorbed on anionic resin. Adsorbed iron is selectively removed with 7.2N nitric acid. Plutonium is recovered from the resin by reductive elution with 0.6% hydrogen peroxide-1.2N hydrochloric acid reagent. Time requirement is one-half day. See specific sample type.

REAGENTS

Ammonia: gas

Ammonium hydroxide: silica free, 1%, 5%, 10%

Anionic resin: AG 1 × 2, chloride form, 50-100 mesh. Bio-Rad Laboratories

Dichromate-sulfuric acid cleaning solution

Eluting reagent: 0.6% hydrogen peroxide and 1.2N hydrochloric acid

Ethyl alcohol

Hydrochloric acid: concentrated, 6N, 9N, 1.2N

Hydrogen peroxide: 30%

Nitric acid: 7.2N, 4N

Silica sand: spherical-grained, 60-200 mesh, St. Peter strata, Minneapolis, Minnesota

Sulfuric acid: concentrated, 3.6N, 0.36N

Thymol blue, sodium: 0.02%

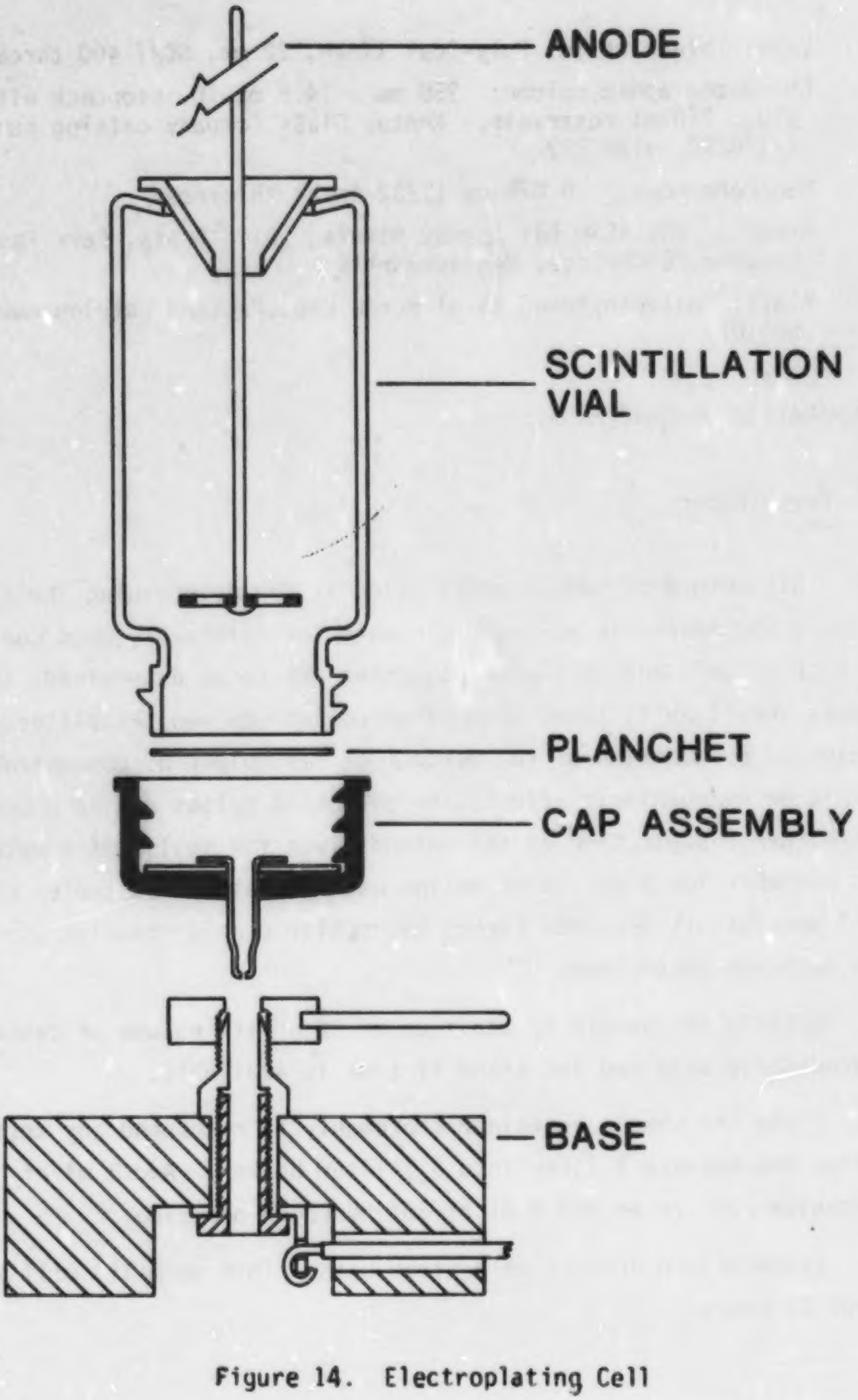

ANODE
SCINTILLATION VIAL
PLANCHET
CAP ASSEMBLY
BASE

Figure 14. Electroplating Cell

APPARATUS (See Figure 14)

Caps: black resin, Poly-Seal liner, 22 mm, GCMI 400 thread design

Chromatographic column: 250 mm × 14.5 mm ID, stopcock with Teflon plug, 250-ml reservoir. Kontes Glass Company catalog number K-420280, size 222

Neoprene sheet: 0.079-cm (1/32-inch) thickness

Rivets: #BS-4830 Dot Speedy Rivets, solid brass, Carr Fastener Company, Cambridge, Massachusetts

Vials: polyethylene, 25-ml screw cap, Packard catalog number 6001075

PREPARATION OF SAMPLE

A. Fresh Water

This method of sample preparation is for determining the sum of soluble and insoluble plutonium in water of relatively good quality. If both soluble and insoluble plutonium are to be determined, the water sample should be filtered soon after collection and the filtered water preserved by addition of two percent of its volume of concentrated nitric or hydrochloric acids. The suspended solids can be prepared for ion-exchange separation by the method given for soils. The method is not suitable for brackish or saline waters inasmuch as sodium chloride will precipitate from the strong hydrochloric acid solution used for ion exchange separation.

1. Acidify the sample by addition of 2% of its volume of concentrated hydrochloric acid and let stand if time is available.

2. Shake the sample container thoroughly to resuspend any settled solids and measure 1 liter into a 1-liter beaker. Add 1 ml of plutonium-236 tracer and 5 ml of 30% hydrogen peroxide.

3. Evaporate to dryness on a steam bath. This normally will take about 20 hours.

4. If the sample has been preserved with nitric acid, add 20 ml of 6N hydrochloric acid and again evaporate to dryness to convert nitrates to chlorides.

5. Moisten the residue with 30% hydrogen peroxide and heat on the steam bath to destroy traces of organic matter.

6. Add 20 ml of 6N hydrochloric acid, cover the beaker with a watch glass, and heat on the steam bath until only flocculent silica remains undissolved.

7. Filter the solution by vacuum through a 47-mm, 0.45-micron membrane filter catching the filtrate in a 150-ml graduated beaker. Use a clean new rubber policeman to loosen the deposit of silica from the beaker and transfer the silica with a minimum amount of 6N hydrochloric acid. Wash the filter several times with small amounts of 6N hydrochloric acid. Cover the beaker containing the filtrate and set it aside.

8. Place the filter in a 100-ml Teflon beaker. Add 10 ml of concentrated nitric acid, cover the beaker, and heat near the boiling point until brown fumes are no longer evolved. This can be best accomplished overnight.

9. Remove the watch glass, add nitric acid to replace any which may have evaporated, and then add 5 ml of 48% hydrofluoric acid. Heat below the boiling point on an asbestos-covered hot plate until the residue is dry and all liquid droplets have evaporated from the sides of the beaker.

10. If organic matter remains, moisten the residue with a few drops of 30% hydrogen peroxide and evaporate to dryness.

11. Add 10 ml of 6N hydrochloric acid and evaporate the solution to dryness. If traces of organic matter remain, moisten the residue with 30% hydrogen peroxide and heat until foaming ceases.

12. Add 5 ml of 6N hydrochloric acid and a drop of 30% hydrogen peroxide. Cover the beaker and heat for 30 minutes to dissolve the residue.

13. Pour the solution into the beaker containing the other portion of the sample solution and rinse the Teflon beaker with 6N hydrochloric acid until the total solution volume is 60 ml. If the volume is greater, evaporate the solution to 60-ml volume. Cover the beaker with a watch glass and hold for the ion-exchange separation of plutonium.

14. Follow Procedure, beginning with Part A, page 113.

B. Sea Water

The following procedure is to determine the sum of soluble and insoluble plutonium in saline water and sea water. The plutonium is coprecipitated on ferric and rare earth hydroxides. The hydroxides are dissolved in 6N hydrochloric acid and the insoluble residue is treated with hydrofluoric and nitric acids.

1. Acidify the sea water sample by the addition of 2% of its volume of concentrated hydrochloric acid.

2. Shake the sample container thoroughly to resuspend any settled solids and measure 1 liter into a 1-liter beaker. Add 1 ml of plutonium-236 tracer. Add 1 ml of 1N sodium metabisulfate.

3. Place a stirring rod in the beaker and heat to the boiling point on a hot plate. Add 5% sodium hypochlorite a drop at a time until the yellow color of free chlorine appears. Add 2 ml of 0.2N ferric chloride carrier and 2 ml of 0.1N yttrium carrier. Stir to mix.

4. While stirring, add concentrated ammonium hydroxide slowly to the hot solution until a precipitate of ferric hydroxide just appears and then add 15 ml of concentrated ammonium hydroxide in excess.

5. Cover the beaker with a watch glass and continue to heat at the simmering point until the precipitate has coagulated. Set the beaker aside to allow the solution to cool and the precipitate to settle. Do not allow the precipitate to settle overnight before proceeding.

6. Remove as much as possible of the supernatant liquid by aspiration through a glass tube into a filtering flask connected to an aspirator pump. Avoid disturbing the precipitate.

7. Transfer the remaining slurry into a 50-ml polypropylene centrifuge tube using 5% ammonium hydroxide to rinse the beaker. The precipitate adhering to the beaker need not be removed at this point. Centrifuge at 2000 rpm for 10 minutes. Decant and discard the supernatant liquid. If the volume of the slurry was greater than the capacity of the centrifuge tube, the remainder may now be transferred to the tube and centrifuged. Do not allow the precipitate to stand any length of time before proceeding.

8. Use about 15 ml of 6N hydrochloric acid to dissolve the precipitate adhering to the beaker and pour this into the centrifuge tube. Shake the tube until the precipitate has dissolved.

9. Filter the solution by vacuum through a 47-mm, 0.45-micron membrane filter into a 150-ml graduated Pyrex beaker. Use a minimum amount of 6N hydrochloric acid to rinse the centrifuge tube and wash the filter several times with small amounts of 6N hydrochloric acid. Cover the beaker and set it aside.

10. Place the membrane filter in a 100-ml Teflon beaker. Add 5 ml of 48% hydrofluoric acid and 5 ml of concentrated nitric acid. Heat on an asbestos-covered hot plate until dry and all liquid droplets have disappeared from the sides of the beaker.

11. Add 5 ml of concentrated nitric acid and again evaporate to complete dryness.

12. Add 10 ml of concentrated nitric acid, cover the beaker with a watch glass and heat until brown fumes are no longer evolved.

13. Remove the watch glass and evaporate the solution to dryness. If traces of organic matter remain, moisten the residue with 30% hydrogen peroxide and heat until foaming ceases.

14. Add 5 ml of 6N hydrochloric acid and a drop of 30% hydrogen peroxide. Cover the beaker and heat until the residue is dissolved.

15. Pour the solution into the 150-ml beaker containing the other portion of the sample solution and rinse the Teflon beaker with 6N hydrochloric acid until the total solution volume is 50 ml. Cover the beaker and hold for the ion-exchange separation of plutonium.

16. Follow Procedure, beginning with Part A, page 113.

C. Urine

Plutonium is coprecipitated on calcium phosphate after digestion of the urine with hydrogen peroxide, hydrochloric acid, and nitric acid. The calcium phosphate is wet-ashed and dissolved in hydrochloric acid.

1. Measure the volume of the urine sample in a graduated cylinder. Record the volume as liters. Pour the sample into a beaker of such size that the beaker will not be more than two-thirds full. Measure a volume (in ml) of concentrated hydrochloric acid equal to 40 times the sample volume in liters (40 ml/liter) and use this successively to rinse the cylinder and the sample container. Add the acid rinse to the beaker. Rinse the cylinder and sample container with a small amount of water and add the rinses to the beaker.

2. Measure a volume in ml of concentrated nitric acid equal to 60 times the sample volume in liters (60 ml/liter) and use this to rinse the cylinder. Pour this into the sample container but do not add it to the beaker until later. Rinse the cylinder with a small amount of water and add the water rinse to the nitric acid in the sample container. Set the sample container aside.

3. Add 1 ml of plutonium-236 internal standard solution. Add 10 ml of 1N calcium chloride. Add a volume of 30% hydrogen peroxide equal to the volume of hydrochloric acid previously added (40 ml/liter).

4. Place a Teflon stirring rod in the beaker and heat to the boiling point on a hot plate. When foaming subsides, cover the beaker with a watch glass and allow the sample to simmer for one hour.

5. Add the nitric acid solution from the sample container to the beaker, cover the beaker with a watch glass, and continue heating at the simmering point for another hour.

6. While stirring the hot solution, add concentrated ammonium hydroxide slowly until a precipitate just appears and then add a volume of concentrated ammonium hydroxide equal to the volume of nitric acid previously added (60 ml/liter). Cover the beaker and set it aside to cool until the precipitate has settled. If time is available, the precipitate may be allowed to settle overnight.

7. Remove as much as possible of the supernatant liquid by aspiration through a glass tube into a filtering flask connected to an aspirator pump. Avoid disturbing the precipitate.

8. Transfer the slurry which remains into a 50-ml polypropylene centrifuge tube using 5% ammonium hydroxide to rinse the beaker. The precipitate adhering to the beaker need not be removed at this point. Centrifuge at 2000 rpm for 10 minutes. Decant and discard the supernatant liquid. If the volume of the slurry was greater than the capacity of the centrifuge tube, the remainder may now be transferred to the tube and centrifuged.

9. Use about 10 ml of concentrated nitric acid to dissolve the precipitate adhering to the beaker and pour this into the centrifuge tube. Replace the cap and shake the tube until the precipitate has dissolved. Pour the solution into a 250-ml graduated beaker. Rinse the centrifuge tube with about 5 ml of concentrated nitric acid.

10. Cover the 250-ml beaker with a watch glass and place it on a hot plate set at a high enough temperature to volatilize the nitric acid with the beaker covered. If the time schedule permits, this digestion may be conducted overnight at the simmering point.

11. When the residue is nearly dry, remove the watch glass and allow the remaining acid to evaporate. If the residue has a yellow or brown color due to organic matter, cool the beaker and moisten the residue with 30% hydrogen peroxide. Cover the beaker and heat until foaming ceases and the residue is again dry. It may be necessary to use nitric acid and hydrogen peroxide alternately with intervening evaporations to dryness in order to obtain a white ash.

12. Add 50 ml of 6N hydrochloric acid and evaporate to approximately 25 ml to remove nitrates and to hydrolyze polyphosphates.

13. Add 6N hydrochloric acid until the volume of sample solution is 50 ml. Cover the beaker with a watch glass and set it aside for the ion-exchange separation of plutonium.

14. Follow Procedure, beginning with Part A, page 113.

D. Tissue Ash

Animal tissues are usually ignited at temperatures not exceeding 550° C to avoid fusion of the ash and may still contain unburned carbon when submitted for analysis. Rumen contents and lung will contain considerable amounts of siliceous mineral matter. Samples which dissolve in 6N hydrochloric acid leaving only a trace of insoluble inorganic matter and no carbon can be treated in the same manner as bone ash. The following directions, although usable for all types of animal tissue ash, apply primarily to those samples containing carbon.

1. Weigh 1 gram of ash into a tared 150-ml graduated glass beaker. A Teflon beaker is not used at this point because carbon adheres annoyingly to Teflon.

2. Add 25 ml of 6N hydrochloric acid. Add 2 to 4 pCi of plutonium-236 tracer.

3. Cover the beaker with a watch glass and heat near but below the boiling point on a hot plate for one hour or longer to leach soluble components from the ash. Set the beaker aside to cool.

4. Filter the solution by vacuum through a 47-mm, 0.45-micron membrane filter into a 100-ml Teflon beaker. Rinse the beaker with a minimum amount of 6N hydrochloric acid using an ultrasonic bath if necessary to dislodge particulate matter. Wash the filter repeatedly with small amounts of 6N hydrochloric acid until the filtrate volume is approximately 50 ml.

5. Pour the filtrate from the Teflon beaker back into the 150-ml beaker. Rinse the Teflon beaker with a minimum amount of 6N hydrochloric acid and set it aside for reuse.

6. Evaporate the solution in the 150-ml Pyrex beaker to 40 ml, cover the beaker and set it aside.

7. Place the filter in a 25-ml platinum evaporating dish and use a few drops of water to transfer any particles adhering to the filter funnel. Dry the filter under a heat lamp.

8. Moisten the filter with ethyl alcohol and ignite. When the alcohol has burned off, ignite the residue in a muffle furnace (600° C) until the carbon has burned off. If there are persistent carbon specks, it may be helpful to cool the dish, moisten the residue with a few drops of water or 3N nitric acid, dry, and then reignite.

9. If any of the residue is loose, transfer it in the dry form to the 100-ml Teflon beaker. Dissolve adherent residue by warming with 5 ml of concentrated nitric acid and 10 ml of 48% hydrofluoric acid. Pour the solution into the Teflon beaker and rinse the platinum dish with a small amount of 4N nitric acid.

10. Evaporate the solution in the Teflon beaker to dryness on an asbestos-covered hot plate and continue heating until all liquid droplets have evaporated from the sides of the beaker.

11. Add 10 ml of 6N hydrochloric acid and evaporate to complete dryness. Repeat the evaporation two more times with 10 ml portions of 6N hydrochloric acid to assure removal of fluoride ion.

12. Add 10 ml of 6N hydrochloric acid and 3 drops of 30% hydrogen peroxide, cover the beaker and heat for 30 minutes to dissolve the residue.

13. Pour the solution from the Teflon beaker into the beaker containing the other portion of the dissolved sample and rinse the Teflon beaker with 6N hydrochloric acid until the total solution volume is 60 ml. If the volume is greater, evaporate to 60 ml. Cover the beaker and hold for the ion-exchange separation of plutonium.

14. Follow Procedure, beginning with Part A, page 113.

E. Bone Ash

The bone ash is dissolved in 6N hydrochloric acid and filtered. The filter containing the insoluble residue is wet-ashed and treated with hydrofluoric acid to remove silica, organic matter, and traces of carbon. The solubilized residue and initial solution are combined.

1. If the bone ash sample is grey due to traces of unburned carbon, weigh 1 to 10 grams into a tared porcelain crucible and ignite in a muffle furnace (700° C) until the ash is uniformly white. Transfer the ignited ash into a 100-ml Teflon beaker. A well ashed sample can be weighed directly into a tared 100-ml Teflon beaker.

2. Add 20 ml of 6N hydrochloric acid plus an additional 2 ml for each gram of ash in excess of 1 gram. Add 1 ml of plutonium-236 internal standard solution. Add 3 drops of 30% hydrogen peroxide.

3. Cover the beaker with a watch glass and heat on an asbestos-covered hot plate until the ash has dissolved and only a trace of dust or carbon remains undissolved. Set aside to cool.

4. Filter by vacuum through a 47-mm, 0.45-micron membrane filter catching the filtrate in a 150-ml graduated beaker. Rinse the Teflon beaker with a minimum amount of 6N hydrochloric acid and wash the filter with 6N hydrochloric acid until the total filtrate volume is 45 to 50 ml. Cover the beaker with a watch glass and set the beaker aside.

5. Place the membrane filter in the Teflon beaker. Add 10 ml of concentrated nitric acid, cover the beaker with a watch glass and heat until brown fumes are no longer evolved and specks of carbon have dissolved. If time is available, the digesti[illegible]ould be continued overnight.

6. Remove the watch glass, add nitric acid [illegible]ace any which may have evaporated, and then add 5 ml of 48% hydr[illegible]ic acid. Evaporate until the residue is dry and all liquid droplets have disappeared from the sides of the beaker.

7. If organic matter remains, moisten the residue with a few drops of 30% hydrogen peroxide and evaporate to dryness.

8. Add 10 ml of 6N hydrochloric acid and evaporate until the residue and beaker are completely dry.

9. Add 5 ml of 6N hydrochloric acid and a drop of 30% hydrogen peroxide. Cover the beaker with a watch glass and heat for 30 minutes to dissolve the residue.

10. Pour the solution into the beaker containing the previously dissolved portion of the sample and rinse the Teflon beaker with 6N hydrochloric acid until the total solution volume is 60 ml. If the volume is greater, evaporate to 60 ml. Cover the beaker with a watch glass and set it aside for the ion-exchange separation of plutonium.

11. Follow Procedure, beginning with Part A, page 113.

PROCEDURE

A. Final Preparation of Sample Solution

1. Note the volume of the prepared solution of the sample in 6N hydrochloric acid and add an equal volume of concentrated hydrochloric acid to adjust the acidity to 9N. Stir to mix. If a white precipitate of sodium chloride appears, increase the volume of the solution by adding

9N hydrochloric acid and warm the solution on a hot plate until the precipitate redissolves.

2. Add 1 drop of 30% hydrogen peroxide for each 10 ml of solution volume and stir to mix. Cover the beaker and place on a hot plate to allow the temperature of the solution to rise at least to 80° C but not to the boiling point. (Bubbles of oxygen will rise in the solution as the excess hydrogen peroxide decomposes and should not be confused with boiling.) Remove the beaker from the hot plate and let it stand overnight. If the ion-exchange separation is to be performed the same day, heat the solution at 80° or 90° C for 1 hour and then let it cool to room temperature.

B. Column Operation

3. Equilibrate the resin by filling the column reservoir with 9N hydrochloric acid and allowing it to drain at 1 drop/sec.

4. Pour the sample solution into the reservoir and rinse the beaker with a minimum amount of 9N hydrochloric acid. Adjust the flow rate to 1 drop/2 sec.

5. When the sample solution has passed through the column, rinse down the sides of the reservoir with about 15 ml of 9N hydrochloric acid and allow to drain. Repeat the rinse two times with 15-ml portions of 9N hydrochloric acid.

6. Close the stopcock. Rinse down the sides of the reservoir with about 15 ml of 7.2N nitric acid and readjust the flow to 1 drop/4 sec. When drained, repeat with a second 15 ml of 7.2N nitric acid and, when this has drained, pour 70 ml of 7.2N nitric acid into the reservoir and check for proper flow rate.

7. Use 5 ml of 1.2N hydrochloric acid to wash down most of the nitric acid from the sides of the reservoir. Do not exceed 10 ml for this purpose. When this has drained, the column is ready for elution of plutonium.

8. Replace the receiving beaker with a clean 50-ml beaker. Pour 50 ml of freshly prepared 0.6% hydrogen peroxide-1.2N hydrochloric acid eluting reagent into the reservoir and adjust the flow rate to 1 drop/2 sec. The flow rate may slow down due to expansion of the resin but need not be readjusted unless the flow stops completely. Collect 45 ml of the eluate.

9. Evaporate the plutonium-containing eluate to dryness on a hot plate which is set low enough to prevent boiling. To avoid bumping and possible loss of sample, stir to mix the heavier nitric acid which layers at the bottom. If a Teflon stirring rod is used, it can be withdrawn without loss of sample and without need for rinsing.

10. Add 0.5 ml of concentrated sulfuric acid and 2 ml of concentrated nitric acid. Cover the beaker and heat on a hot plate until the nitric acid refluxes to the top of the beaker and drips from the watch glass. Move the beaker to a cooler part of the hot plate, remove the watch glass and allow the nitric acid to evaporate. Continue to heat the beaker until the sulfuric acid refluxes part way up the beaker. All the nitric acid must be removed but avoid volatilizing any appreciable amount of the sulfuric acid. Replace the watch glass and set the beaker aside to cool.

C. Electrodeposition

11. Add 3 ml of water to the cool sulfuric acid solution. Replace the watch glass and warm the solution for a minute or two on a hot plate and then allow to cool.

12. Add 4 drops of 0.02% thymol blue sodium salt. Neutralize the solution to the salmon-pink endpoint (pH 2) by blowing gaseous ammonia over the surface while swirling the solution. If the endpoint is overstepped to a yellow color, add 3.6N sulfuric acid a drop at a time until the solution turns pink.

13. Pour the neutralized solution into the plating cell. (See "Construction and Assembly of Electrodeposition Cell," page .) Draw 6 ml of 3.6N sulfuric acid into a pipette and use this in small increments to rinse the beaker three or more times.

14. Neutralize the solution again to pH 2 with gaseous ammonia. The solution should have a straw color when viewed from the top and a slight pinkish cast when viewed through the sides of the cell. If the endpoint is overstepped, use 3.6N sulfuric acid a drop at a time to return the solution to the proper color.

15. Lower the platinum anode into the solution until the bottom edge of the anode is about 2 mm above the shoulder of the cell. If set too deep, gas bubbles will be trapped and cause fluctuation of the current. When the current is first turned on, it will be about 0.8 ampere. As the solution warms the current will increase and must be readjusted to 1.2 amperes when it rises above this value. After 15 to 30 minutes the current will stabilize and electrolysis can be allowed to continue at 1.2 ampere without attention for a total electrolysis time of 1.5 to 2 hours.

16. Without cutting off the current, add 10 ml of 10% ammonium hydroxide and continue the electrolysis for 1 minute. Lift the anode out of the cell and then switch off the current. Pour the solution out of the cell and rapidly flood the cell three times with 1% ammonium nitrate 1% ammonium hydroxide solution. Disassemble the cell and quickly wash the planchet with a stream of alkaline ethyl alcohol. Touch a piece of filter paper to the edge of the planchet to adsorb the film of alcohol.

17. Write the last two digits of the sample number on the bottom of the planchet, place it in a cupped planchet and heat for 10 minutes on a hot plate.

D. Determination of Electrodeposition Recovery

18. Pour the alkaline electrolyte from the cell back into the 50-ml beaker and add the cell rinses to the beaker. After removal of the planchet, cap the cell with a Polyseal cap. Rinse the cell with 5 ml of concentrated hydrochloric acid, 5 ml of concentrated nitric acid, and a small amount of water. Add these rinses to the beaker.

19. Evaporate on a steam bath until only sulfuric acid remains. Repeat the electrodeposition as given under Section C.

20. Compute recovery as follows:

$$R = \frac{a - b}{a}$$

where R = fractional recovery in the first electrodeposition

a = activity in cpm of first planchet

b = activity in cpm of second planchet

PREPARATION OF ION-EXCHANGE COLUMN

The following directions for the preparation of ion exchange columns apply to the adsorption of plutonium from 9N hydrochloric acid solution.

1. Roll some glass wool into a loose ball and push it to the bottom of the column with a glass rod. Wash loose fibers down with water and pack the glass wool tightly with the rod. The glass wool plug should have a depth of about 1 cm. Run water through the plug until air bubbles are displaced and then drain the water just to the top of the plug. Add 20 ml of water and mark the column at the 20-ml level. Drain the water but leave a small amount above the plug.

2. Wash the resin repeatedly by decantation until the supernatant water is free of foam and turbidity. Add a volume of concentrated hydrochloric acid equal to one-tenth the volume of resin slurry.

3. Using a 20 or 25-ml pipette held upside down, stir the resin slurry and draw some into the pipette. If the slurry is too thick, dilute it with 1.2N hydrochloric acid. Add resin slurry to the column and pack it by opening the stopcock briefly until the column contains 20 ml of packed resin. Maintain a layer of 1.2N hydrochloric acid above the resin to prevent air from being drawn into the resin bed. Wash down any resin particles from the reservoir with 1.2N hydrochloric acid and use the glass rod to loosen any particles adhering to the sides of the column.

4. When the resin particles have completely settled, slowly pour in dry sand through a layer of liquid to a depth of 1.5 cm. The capillarity of the samd stops the flow of liquid and prevents air from entering the resin bed.

5. Using a wash bottle, wash down the sides of the reservoir with 20 to 30 ml of concentrated hydrochloric acid and let the acid drain at 1 drop/sec.

6. Fill the reservoir to the top with 1.2N hydrochloric acid and let it drain at 1 drop/sec.

7. Close the stopcock and add a few milliliters of 1.2N hydrochloric acid.

CONSTRUCTION AND ASSEMBLY OF ELECTRODEPOSITION CELLS

Cross contamination during preparation of thin sources by electrodeposition is minimized by the use of low-cost, disposable cells. The cells can be cleaned for reuse if the activity level does not vary greatly from sample to sample.

A. Construction

1. Cut a 1.43-cm (9/16-inch) hole in the bottom of the polyethylene vial with a sharp cork borer. Improve the seal by abrading the threaded end with wet #320 waterproof emery paper held against a flat surface. Finish with wet #600 emery papers.

2. Remove the polyethylene liner from a 22-mm Poly-Seal cap. With a cork borer or leather punch, cut out the polyethylene tube from the liner. The conical part of the liner is used as a cover for the cell to minimize escape of spray.

3. Drill a 0.355-cm (0.140-inch, #28 drill) hole through the center of the cap. Bevel the edge of the hole on the inside of the cap with a reamer.

4. Cut a 1.91-cm (3/4-inch) disc from 0.079-cm neoprene sheeting with a cork borer or a die. Cut a 0.317-cm (1/8-inch) hole in the center of the disc with a cork borer or leather punch.

5. Place the washer in the cap and pass the shank of the rivet through the washer and the hole in the cap.

B. Cleaning

6. Remove any surface film of oil from the polyethylene body of the cell with acetone followed by water.

7. Completely immerse the body of the cell in dichromate-sulfuric acid cleaning solution for 2 to 3 hours. Rinse off the cleaning solution with water and immerse the cell in 4N nitric acid for at least one hour. Rinse and immerse in distilled water until ready to use.

8. The cleaning process renders the polyethylene hydrophilic, provided the cell is kept continuously wet after having been cleaned. The polyethylene parts of used cells can be rinsed and then cleaned by the directions given in step 7 except that the immersion in dichromate

sulfuric acid cleaning solution is limited to one hour. Clean the caps and neoprene washers by immersing for a few minutes in 4N nitric acid and then rinse with water.

C. Assembly

9. Connect one hole of a 2-hole #6 rubber stopper to an aspirator pump with a length of rubber tubing.

10. Rinse the polyethylene cell with distilled water but do not dry. Hold the planchet centered against the threaded end of the cell and place the rubber stopper against the other end of the cell. Apply suction by placing a finger over the open hole of the stopper. The vacuum will hold the planchet in a centered position while the cap assembly is screwed on. Fill the cell half way with water and alternately apply and release the vacuum. The flexing will cause the planchet to seat more firmly against the cell. Check to see that no stream of air bubbles rises through the water when vacuum is applied. If the vacuum is great enough, the water may boil but the boiling is easily distinguished from air leakage.

11. Fill the assembled cell to the top with water to preserve the hydrophilic character of the cell until ready to add the sample.

STANDARDIZATION AND CALCULATION

A. Plutonium-239 Standard

1. Prepare the plutonium-239 standard as an 8N nitric acid solution containing about 200 pCi/ml. At this acid concentration, the plutonium is in the form of an anionic complex and is not likely to adsorb on glass. The activity of the solution is low enough that a 1-ml or larger pipette can be used.

2. Calculate the effective activity for use as an alpha spectrometric standard. Example: An Amersham standard certified to contain 1.000 µCi of plutonium-239 was stated to contain plutonium-240 equal to 3.7% of the plutonium-239 activity. Inasmuch as the abundance of the 5.11 and 5.16 MeV alphas of plutonium-239 is 99% and the 5.12 ard 5.17 MeV alphas of plutonium-240 are not resolved, the effective activity was 0.99 + 0.037 µCi. The standard was diluted with 8N nitric acid to give a plutonium-239 activity of 200 pCi/ml. The effective activity for use as an alpha spectrometric standard was 205.4 pCi/ml and, when corrected for an analyzed loss during initial dilution, the activity was 205.33 pCi/ml.

B. Plutonium-236 Tracer Standard (See Appendix C.)

3. Prepare the plutonium-236 as a 6N hydrochloric acid solution containing about 200 pCi/ml. This solution is standardized against plutonium-239 and preserved as a stock solution.

4. Accurately dilute an aliquot of the stock solution to 200 ml with 6N hydrochloric acid to give a solution containing about 4 pCi/ml.

C. Standardization of Plutonium-236

5. Transfer 1 ml each of plutonium-239 standard solution and plutonium-236 stock solution to a 50-ml beaker and evaporate to dryness. Electrodeposit twice to obtain electrodeposition recovery.

6. For a 1% relative standard deviation in the standardization, count the first planchet to accumulate 20,000 counts for both the plutonium-239 and plutonium-236 peaks. For 200 pCi of each, this will require two 80 or 100 minute counts.

7. Calculate the activity of the plutonium-236 stock solution as follows:

$$\text{Plutonium-236 (pCi/ml)} = \frac{BCV_a}{AV_b}$$

where B = gross counts in channels encompassed by the plutonium-236 peak

C = effective activity of the plutonium-239 standard solution (pCi/ml)

V_a = volume of plutonium-239 standard solution taken for electrolysis (ml)

A = gross counts in channesl encompassed by the plutonium-239 peak

V_b = volume of plutonium-236 stock solution taken for electrolysis (ml)

D. Calculation of Recovery

8. Count the second planchet for 1000 minutes and calculate the electrodeposition recovery for the first planchet. Calculate the counts per minute per pCi of plutonium-236 which should have been obtained.

E. Calculation of Detector Efficiency and Yield

9. Count the second planchet for 1000 minutes and calculate the fraction of plutonium-239 recovered on the first planchet. Calculate the fractional detector efficiency as follows:

$$\text{Efficiency (cpm/pCi)} = \frac{A}{TCR}$$

where A = gross counts in channels encompassed by the plutonium-239 peak of the first planchet

T = counting time (minutes)

C = effective activity of plutonium-239 in the volume taken for electrodeposition (pCi)

R = fractional electrodeposition recovery on the first planchet

10. The detector efficiency does not enter into sample calculations when using plutonium-236 as a tracer standard. It serves as a check on detector performance and is required for the calculation of plutonium yield which in turn serves as a check on the analysis. The plutonium yield in an analysis is calculated as follows:

$$\text{Yield (\%)} = \frac{B}{TFED} \times 100$$

where B = gross counts in channels encompassed by the plutonium-236 peak

T = counting time (minutes)

F = plutonium-236 activity added to sample (pCi)

E = fractional detector efficiency

D = fractional decay of plutonium-236 between time of standardization and time of sample count

F. Calculation of Sample Activity

11. Calculate the plutonium-239 activity in pCi/g, pCi/kg, pCi/liter, or pCi/m^3 as follows:

$$\text{Plutonium-239 (pCi/unit)} = \frac{\left(\frac{AFD}{B}\right) - \left(\frac{A_1FD_1}{B_1}\right)}{\text{sample size}}$$

where A = gross counts for sample planchet which appear in the channels normally encompassed by a plutonium-239 peak containing 10,000 counts

F = plutonium-236 activity added to sample and reagent blank (pCi)

D = fractional decay of plutonium-236 between time of standardization in days and time of count $= e^{-0.0006665 \times \text{days}}$

B = gross counts for sample planchet which appear in the channels normally encompassed by a plutonium-236 peak containing 10,000 counts

A_1 = gross counts, as above, for reagent blank

D_1 = fractional decay of plutonium-236, as above, for reagent blank

B_1 = gross counts, as above, for reagent blank

Plutonium-238 is calculated by the same equation.

G. Calculation of Error

12. Calculate the two-sigma standard deviation as follows:

$$2\,\sigma\ (\text{pCi/unit}) = \frac{2\sqrt{\left(\frac{1}{A} + \frac{1}{B}\right)\left(\frac{AFD}{B}\right)^2 + \left(\frac{1}{A_1} + \frac{1}{B_1}\right)\left(\frac{A_1 F D_1}{B_1}\right)^2}}{\text{sample size}}$$

The terms are the same for sample calculations (Part F, step 11).

DETERMINATION OF POLONIUM-210 AND LEAD-210 IN SOIL OR AIR FILTERS

PRINCIPLE OF THE METHOD

This procedure utilizes the self-deposition of polonium onto a nickel disc in an acid medium. Interferences are held to a minimum. The polonium-210 is determined by alpha spectroscopy. Lead-210 is determined by its daughter, polonium-210.

REAGENTS

Ammonium hydroxide: concentrated
Citric acid: 40%
Hydrochloric acid: concentrated, 0.5N
Hydrofluoric acid: 48%
Hydroxylamine hydrochloride: 100 g/100 ml
Lead carrier: 10 mg Pb/ml in 4N nitric acid
Polonium-208 tracer: 3.5 pCi/ml in 4N nitric acid
Thioacetamide: 10%

APPARATUS

Deposition cells with nickel disc (Figure 14)
Steam bath with stirrer

PROCEDURE

1. Weigh 0.5 to 1.0 grams dried soil, or 1/4 of an air filter, in a 100-ml Teflon beaker. Keep filter as flat and close to bottom as possible. Add 1 ml polonium tracer and 1 ml lead carrier.

2. Add 10 ml concentrated nitric acid and 10 ml 48% hydrofluoric acid and place on hot plate, taking care not to volatilize polonium (do not boil). Repeat 4 times.

3. Add 10 ml concentrated nitric acid and evaporate to dryness. Repeat 3 times.

4. Add enough concentrated nitric acid and heat to loosen insolubles. Add 10 ml water and filter through a Whatman #42 filter in a disposable funnel into a disposable 50-ml centrifuge tube. Wash filter with 10 ml water followed by 10 ml 0.5N hydrochloric acid.

5. Evaporate the solution in the centrifuge tube to dryness in a steam bath. Re-dissolve with 1 ml concentrated hydrochloric acid. Add 10 ml water and adjust pH to 3.5-4.0 with hydrochloric acid and/or ammonium hydroxide.

6. Add 5 ml of 10% thioacetamide solution and digest for 1 to 2 hours on the steam bath. Cool.

7. Centrifuge. Decant and discard the supernatant liquid. Dissolve the precipitate with 1 ml concentrated hydrochloric acid. Repeat steps 5 and 6.

8. Dissolve the residue with 1 ml concentrated hydrochloric acid in the steam bath and add 5 ml water and filter through a Whatman #42 filter (using a disposable funnel) into a new 50-ml disposable graduated centrifuge tube. Wash filter with 1 ml water and 1 ml 0.5N hydrochloric acid.

9. Transfer to a deposition cell with a minimum of water and add 2 ml 40% citric acid solution and 2 ml hydroxamine hydrochloride. Add water until cell is 3/4 full. Place cell in hot water bath-stirrer at 80° C. Stir for 2½ to 3 hours.

10. Transfer solution back to centrifuge tube and wash cell with water. Collect the washing in the centrifuge tube. Save solution for 30 days (ingrowth for lead-210 analysis). See steps 13 and 14.

11. Wash the deposition cell with ethyl alcohol, discarding wash. Dismantle cell and wash nickel disc with ethyl alcohol.

12. Heat the disc (in an aluminum planchet) on a hot plate (200° to 300° C) for 20 minutes. Cool and count in an alpha spectrometer.

13. After 30 days reduce volume of solution saved in step 10 to 10 ml in steam bath.

14. Add 1 ml hydroxamine hydrochloride and transfer to a deposition cell and proceed with steps 9 through 12.

CALCULATIONS

A. Polonium

$$\text{Efficiency (\%)} = \frac{\frac{A}{C} - \frac{B}{D}}{N e^{-\lambda t}}$$

where A = gross sample counts of polonium-208

B = gross background counts of polonium-208

C = elapsed sample counting time (min)

D = elapsed background counting time (min)

N = activity in pCi of polonium-208 on Julian date 1

$$e^{-\lambda t} = e^{-\frac{0.693}{1069.45} \times \text{days}}$$

Calculate activity of sample on counting date by the following equation:

$$\text{Polonium-210 (pCi/unit)} = \frac{\frac{E}{C} - \frac{F}{D}}{\text{efficiency} \times V_s}$$

where E = gross sample counts of polonium-210

F = gross background counts of polonium-210

V_s = quantity of sample in units to be reported

Sample data are reported at sample separation date. Calculate activity on this date:

$$\text{Polonium-210 at } t_1 \text{ (pCi/unit)} = \frac{\text{polonium-210 at } t_2}{e^{-\lambda t_2 - t_1}}$$

where $e^{-\lambda} = e^{-\frac{0.693}{138.4}}$

$t_2 - t_1$ = time elapsed between separation and counting

Calculate counting error at time of counting:

$$2\sigma = \frac{2}{\text{efficiency} \times V_s} \left[\frac{\frac{E}{C} - \frac{F}{D}}{\frac{A}{C} - \frac{B}{D}}\right] \sqrt{\left[\frac{\frac{E}{C^2} + \frac{F}{D^2}}{\left(\frac{E}{C} - \frac{F}{D}\right)^2}\right] + \left[\frac{\frac{A}{C^2} + \frac{B}{D^2}}{\left(\frac{A}{C} - \frac{B}{D}\right)^2}\right]}$$

Calculate counting error at the time of separation:

$$2\sigma = \frac{2\sigma \text{ at time of counting}}{e^{-\lambda(t_2 - t_1)}}$$

where $e^{-\lambda} = e^{-\frac{0.693}{138.4}}$

B. Lead-210

Lead is calculated by allowing its granddaughter polonium-210 to ingrow for thirty days. The counting efficiency used is that found by counting a plutonium-239 standard in the alpha spectrometer and is calculated as cpm/pCi. The fractional yield is that determined by atomic absorption analysis on the final deposition solution and dividing the recovered lead by the carrier size.

Calculate the activity at the time of the second counting (t_3):

$$\text{Lead-210 at } t_3 \text{ (pCi/unit)} = \frac{\frac{J}{K} - \frac{E}{D}}{\text{eff} \times Y \times V_S}$$

Calculate the counting error:

$$2 = \frac{2}{\text{eff}\quad Y\quad V_S} \sqrt{\frac{\frac{J}{K} + \frac{F}{D}}{K}}$$

where J = gross sample counts of polonium-210 at second polonium counting

K = elapsed time of second polonium count

eff = fractional efficiency (cpm/pCi)

Y = fraction of lead recovered

Calculate the activity at the time of the second separation (t_2):

$$\text{Lead-210 at } t_2 \pm 2\sigma \text{ (pCi/unit)} = \frac{\text{lead-210 at } t_3 \pm 2\sigma \text{ at } t_3}{e^{-\lambda(t_3 - t_2)}}$$

where t_3-t_2 = elapsed time between second sample counting and separate separation

$$e^{-\lambda} = e^{-\frac{0.693}{7446}}$$

Calculate the activity of lead-210 at the time of original separation:

$$\text{Lead-210 at } t_1 \pm 2\sigma \text{ at } t_1 = \frac{\lambda_{\text{Po-210}}}{\lambda_{\text{Pb-210}}} \; \frac{\text{Pb-210 at } t_2 \pm 2\sigma \text{ at } t_2}{1 - e^{-\lambda(t_2 - t_1)}}$$

where t_2-t_1 = time elapsed between original separation and second sample separation

APPENDIX A. REAGENT PREPARATION

Alcohol-Hydrochloric Acid

Add 10 ml concentrated hydrochloric acid to 100 ml absolute ethyl alcohol.

Ammonium Acetate Buffer, pH 5.2

Dissolve 153 g ammonium acetate in 800 ml distilled water, add 28.6 ml of glacial acetic acid. Adjust to pH 5.2 using either ammonium hydroxide or acetic acid. Dilute to 1000 ml with distilled water.

Ammonium Dichromate

1.0M - Dissolve 252 g of ammonium dichromate in distilled water. Adjust pH to 6.5 with ammonium hydroxide or nitric acid, and dilute to 1000 ml with distilled water.

0.1M - Same as 1.0M only use 25.2 g of ammonium dichromate.

Complexing Solution

Dissolve 216 g of disodium-ethylenediaminetetraacetate in 250 ml water. Add 10 ml Sr^{2+} carrier (40 mg/ml), 10 ml Ba^{2+} carrier (40 mg/ml), and 200 ml ammonium acetate buffer (pH 5.2). Adjust the pH to 5.20 using approximately 70 ml 6N ammonium hydroxide, dilute to 3 liters with water. (Re-check pH before using.)

Ether-Hydrochloric Acid

In an ice-bath, add equal volumes of concentrated hydrochloric acid and diethyl ether.

Nitric-Perchloric Acid

Prepare by adding 162 ml 70% perchloric acid to 838 ml concentrated nitric acid.

Ethylenediaminetetraacetate, Disodium

EDTA, disodium - Dihydrate, powder.

3%w - Dissolve 33.3 g of disodium EDTA in 900 ml of distilled water, adjust to pH 5.2 with ammonium hydroxide and dilute to 1000 ml with distilled water. Recheck pH just prior to using.

6% - Dissolve 60 g disodium EDTA in 900 ml water and dilute to 1 liter.

2% - Dissolve 20 g disodium EDTA in 900 ml water and dilute to 1 liter.

Liquid Scintillation Solution (for tritium)

Dissolve 8.0 g 2,5-diphenyloxazole (PPO), 1.5 g p-bis-(o-methylstyrl)-benzene (BIS-MSB), and 120 g napthalene in 800 ml spectrographic-grade p-dioxane and dilute to 1 liter. Store in amber bottle. The solution is not usable after one month.

Liquid Scintillation Solution (for noble gas)

Dissolve 1.5 g 1.5 diphenyloxazole (PPO) and 300 mg 1,4-bis-2-(4-methyl-5-phenyloxazole)-benzene (dimethyl-POPOP) in 800 ml toluene and dilute to 1 liter with toluene. Store in an amber bottle. The solution is not usable after one month.

Liquid Scintillation Solution (for carbon-14)

Dissolve 17.5 g of 2,5-diphenyloxazole and 3.75 g of p-bis-(o-methylstryrl)-benzene in 500 ml of spectrographic-grade benzene.

Nicholson's Flux

Weigh: 65.8 g potassium carbonate
50.5 g sodium carbonate
33.7 g sodium tetraborate decahydrate
30 mg barium sulfate

into a 500-ml platinum dish. Mix and fuse. Cool and grind to pass a 10-mesh screen.

Sodium Acetate Buffer, pH 3.6

Dissolve 200 g sodium acetate in 500 ml water. Add 385 ml acetic acid. Adjust pH to 3.6 with ammonium hydroxide. Dilute to 1 liter.

Strontium Carrier

40 mg/ml - Dissolve 96.6 g strontium nitrate in 800 ml distilled water. Dilute to 1000 ml with distilled water.

Standardization:

Pipet 5 ml of carrier solution into a 40-ml centrifuge tube, and dilute to 20 ml with distilled water. Make alkaline with ammonium hydroxide and heat to near boiling in a water bath. Add 10 ml 1N ammonium oxalate, and cool in an ice bath. Filter the solution through a tared, sintered glass filter or Millipore type OH filter. Wash the precipitate with three 10-ml portions distilled water, three 10-ml portions 95% ethyl alcohol, and three 10-ml portions diethyl ether. Place in a desiccator until constant weight is achieved. Weigh as $SrC_2O_4 \cdot H_2O$.

Lead Carrier

100 mg Pb/ml - Dissolve 159.9 g lead nitrate in 800 ml distilled water, and dilute to 1000 ml.

Calcium Carrier

2M - Dissolve 328.2 g calcium nitrate in distilled water, and dilute to 1000 ml.

Barium Carriers

40 mg/ml - Dissolve 76.2 g barium nitrate in 800 ml distilled water, and dilute to 1000 ml.

10 mg/ml - Use 19.0 g barium nitrate.

5 mg/ml - Use 9.5 g barium nitrate.

1 mg/ml - Use 1.9 g barium nitrate.

Yttrium Carrier

1 mg/ml - Dissolve 1.23 g yttrium oxalate in a minimum of concentrated nitric acid, and dilute to 1000 ml with distilled water.

Standardization:

Pipet 5 ml carrier solution into a 40-ml centrifuge tube, and dilute to 20 ml with distilled water. Add 10 ml 2N oxalic acid, and adjust the pH to 1.5 with concentrated ammonium hydroxide. Heat to near boiling in a water bath. Cool in an ice bath for 20 minutes. Filter the solution through a tared, sintered-glass filter or Millipore type OH filter. Wash the precipitate with three 10-ml portions distilled water, three 10-ml portions 95% ethyl alcohol, and three 10-ml portions diethyl ether. Place in a desiccator until constant weight is achieved. Weigh as $Y_2(C_2O_4)_3 \cdot 9H_2O$.

Mixed Rare Earth Carrier

Dissolve 96.8 g ferric chloride, 31.0 g cerium nitrate, and 35.3 g zirconium chloride in 800 ml distilled water. Add 1 ml concentrated nitric acid and dilute to 1000 ml.

APPENDIX B. DECAY FACTORS FOR YTTRIUM AND STRONTIUM

Table 1.	Yttrium-90 Decay and Ingrowth Factors (0-72 hours)
Table 2.	Yttrium-90 Ingrowth Factors (0-27 days)
Table 3.	Strontium-89 Decay Factors (0-59.5 days)
Table 4.	Strontium-90 Decay Factors (0-66 years)

Table 1. YTTRIUM-90 DECAY AND INGROWTH FACTORS (0-72 hours)

t (hr)	$e^{-\lambda t}$	$1-e^{-\lambda t}$	t (hr)	$e^{-\lambda t}$	$1-e^{-\lambda t}$	t (hr)	$e^{-\lambda t}$	$1-e^{-\lambda t}$
0.0	1.0000	.0000	24.0	.7717	.2283	48.0	.5955	.4045
0.5	.9940	.0054	24.5	.7676	.2324	48.5	.5923	.4077
1.0	.9893	.0107	25.0	.7634	.2366	49.0	.5891	.4109
1.5	.9839	.0161	25.5	.7593	.2407	49.5	.5860	.4140
2.0	.9786	.0214	26.0	.7552	.2448	50.0	.5828	.4172
2.5	.9734	.0266	26.5	.7512	.2488	50.5	.5797	.4203
3.0	.9681	.0319	27.0	.7471	.2529	51.0	.5766	.4234
3.5	.9629	.0371	27.5	.7431	.2569	51.5	.5735	.4265
4.0	.9577	.0423	28.0	.7391	.2609	52.0	.5704	.4296
4.5	.9526	.0474	28.5	.7351	.2649	52.5	.5673	.4327
5.0	.9474	.0526	29.0	.7311	.2689	53.0	.5642	.4358
5.5	.9423	.0577	29.5	.7272	.2728	53.5	.5612	.4388
6.0	.9373	.0627	30.0	.7233	.2767	54.0	.5582	.4418
6.5	.9322	.0678	30.5	.7194	.2806	54.5	.5552	.4448
7.0	.9272	.0728	31.0	.7155	.2845	55.0	.5522	.4478
7.5	.9222	.0778	31.5	.7117	.2883	55.5	.5492	.4508
8.0	.9172	.0828	32.0	.7078	.2922	56.0	.5462	.4538
8.5	.9123	.0877	32.5	.7040	.2960	56.5	.5433	.4567
9.0	.9074	.0926	33.0	.7002	.2998	57.0	.5404	.4596
9.5	.9025	.0975	33.5	.6965	.3035	57.5	.5375	.4625
10.0	.8976	.1024	34.0	.6927	.3073	58.0	.5346	.4654
10.5	.8928	.1072	34.5	.6890	.3110	58.5	.5317	.4683
11.0	.8880	.1120	35.0	.6853	.3147	59.0	.5288	.4712
11.5	.8832	.1168	35.5	.6816	.3184	59.5	.5260	.4740
12.0	.8785	.1215	36.0	.6779	.3221	60.0	.5232	.4768
12.5	.8737	.1263	36.5	.6743	.3257	60.5	.5203	.4797
13.0	.8690	.1310	37.0	.6706	.3294	61.0	.5175	.4825
13.5	.8644	.1356	37.5	.6670	.3330	61.5	.5148	.4852
14.0	.8597	.1403	38.0	.6634	.3366	62.0	.5120	.4880
14.5	.8551	.1449	38.5	.6599	.3401	62.5	.5092	.4908
15.0	.8505	.1495	39.0	.6563	.3437	63.0	.5065	.4935
15.5	.8459	.1541	39.5	.6528	.3472	63.5	.5038	.4962
16.0	.8413	.1587	40.0	.6493	.3507	64.0	.5010	.4990
16.5	.8368	.1632	40.5	.6458	.3542	64.5	.4983	.5017
17.0	.8323	.1677	41.0	.6423	.3577	65.0	.4957	.5043
17.5	.8278	.1722	41.5	.6388	.3612	65.5	.4930	.5070
18.0	.8234	.1766	42.0	.6354	.3646	66.0	.4903	.5097
18.5	.8189	.1811	42.5	.6320	.3680	66.5	.4877	.5123
19.0	.8145	.1855	43.0	.6286	.3714	67.0	.4851	.5149
19.5	.8101	.1899	43.5	.6252	.3748	67.5	.4825	.5175
20.0	.8058	.1942	44.0	.6219	.3781	68.0	.4799	.5201
20.5	.8014	.1986	44.5	.6185	.3815	68.5	.4773	.5227
21.0	.7971	.2029	45.0	.6151	.3849	69.0	.4747	.5253
21.5	.7928	.2072	45.5	.6118	.3882	69.5	.4722	.5278
22.0	.7885	.2115	46.0	.6085	.3915	70.0	.4696	.5304
22.5	.7843	.2157	46.5	.6053	.3947	70.5	.4671	.5329
23.0	.7801	.2199	47.0	.6020	.3980	71.0	.4646	.5354
23.5	.7759	.2241	47.5	.5988	.4012	71.5	.4621	.5379

Table 2. YTTRIUM-90 INGROWTH FACTORS (0-27 days)

t (days)	$1-e^{-\lambda t}$	t (days)	$1-e^{-\lambda t}$	t (days)	$1-e^{-\lambda t}$
0.00	.0000	9.00	.9029	18.00	.9906
0.25	.0627	9.25	.9090	18.25	.9912
0.50	.1215	9.50	.9147	18.50	.9917
0.75	.1766	9.75	.9201	18.75	.9922
1.00	.2283	10.00	.9251	19.00	.9927
1.25	.2767	10.25	.9298	19.25	.9932
1.50	.3221	10.50	.9342	19.50	.9936
1.75	.3646	10.75	.9384	19.75	.9940
2.00	.4045	11.00	.9422	20.00	.9944
2.25	.4418	11.25	.9458	20.25	.9948
2.50	.4768	11.50	.9492	20.50	.9951
2.75	.5097	11.75	.9524	20.75	.9954
3.00	.5404	12.00	.9554	21.00	.9957
3.25	.5692	12.25	.9582	21.25	.9959
3.50	.5963	12.50	.9608	21.50	.9962
3.75	.6216	12.75	.9633	21.75	.9964
4.00	.6453	13.00	.9656	22.00	.9967
4.25	.6676	13.25	.9678	22.25	.9969
4.50	.6884	13.50	.9697	22.50	.9971
4.75	.7080	13.75	.9716	22.75	.9973
5.00	.7263	14.00	.9734	23.00	.9974
5.25	.7435	14.25	.9751	23.25	.9976
5.50	.7596	14.50	.9766	23.50	.9977
5.75	.7746	14.75	.9781	23.75	.9979
6.00	.7888	15.00	.9795	24.00	.9980
6.25	.8020	15.25	.9808	24.25	.9981
6.50	.8145	15.50	.9820	24.50	.9982
6.75	.8261	15.75	.9831	24.75	.9984
7.00	.8370	16.00	.9842	25.00	.9985
7.25	.8472	16.25	.9852	25.25	.9986
7.50	.8568	16.50	.9861	25.50	.9987
7.75	.8658	16.75	.9870	25.75	.9987
8.00	.8742	17.00	.9878	26.00	.9988
8.25	.8820	17.25	.9886	26.25	.9989
8.50	.8896	17.50	.9893	26.50	.9990
8.75	.8964	17.75	.9900	26.75	.9990
				27.00	.9991

Table 3. STRONTIUM-89 DECAY FACTORS* (0-59.5 days)

t (days)	$e^{-\lambda t}$	t (days)	$e^{-\lambda t}$	t (days)	$e^{-\lambda t}$
0.0	1.0000	20.0	.7620	40.0	.5808
0.5	.9932	20.5	.7569	40.5	.5769
1.0	.9865	21.0	.7518	41.0	.5730
1.5	.9798	21.5	.7568	41.5	.5690
2.0	.9732	22.0	.7416	42.0	.5652
2.5	.9668	22.5	.7366	42.5	.5613
3.0	.9601	23.0	.7317	43.0	.5575
3.5	.9536	23.5	.7267	43.5	.5539
4.0	.9471	24.0	.7218	44.0	.5500
4.5	.9407	24.5	.7169	44.5	.5462
5.0	.9344	25.0	.7120	45.0	.5427
5.5	.9280	25.5	.7072	45.5	.5380
6.0	.9217	26.0	.7023	46.0	.5352
6.5	.9155	26.5	.6977	46.5	.5318
7.0	.9093	27.0	.6930	47.0	.5280
7.5	.9031	27.5	.6882	47.5	.5245
8.0	.8970	28.0	.6836	48.0	.5210
8.5	.8909	28.5	.6790	48.5	.5175
9.0	.8849	29.0	.6742	49.0	.5140
9.5	.8789	29.5	.6699	49.5	.5105
10.0	.8729	30.0	.6651	50.0	.5070
10.5	.8670	30.5	.6608	50.5	.5035
11.0	.8612	31.0	.6562	51.0	.5000
11.5	.8553	31.5	.6519	51.5	.4967
12.0	.8495	32.0	.6473	52.0	.4933
12.5	.8438	32.5	.6430	52.5	.4900
13.0	.8381	33.0	.6388	53.0	.4868
13.5	.8324	33.5	.6342	53.5	.4834
14.0	.8268	34.0	.6300	54.0	.4801
14.5	.8212	34.5	.6259	54.5	.4769
15.0	.8156	35.0	.6215	55.0	.4734
15.5	.8101	35.5	.6172	55.5	.4702
16.0	.8046	36.0	.6131	56.0	.4671
16.5	.7992	36.5	.6090	56.5	.4640
17.0	.7938	37.0	.6050	57.0	.4608
17.5	.7883	37.5	.6009	57.5	.4578
18.0	.7881	38.0	.5968	58.0	.4547
18.5	.7778	38.5	.5928	58.5	.4513
19.0	.7725	39.0	.5888	59.0	.4484
19.5	.7672	39.5	.5848	59.5	.4454

* half-life equals 51 days

Table 4. STRONTIUM-90 DECAY FACTORS (0-66 years)

Months Years	0	3	6	9	12	15	18	21	24	27	30	33
0	1.0000	.9937	.9876	.9814	.9753	.9692	.9631	.9572	.9512	.9452	.9394	.9335
3	.9277	.9219	.9161	.9104	.9047	.8991	.8935	.8879	.8824	.8769	.8714	.8660
6	.8606	.8552	.8499	.8446	.8393	.8341	.8289	.8237	.8186	.8135	.8084	.8033
9	.7983	.7934	.7884	.7835	.7786	.7737	.7689	.7641	.7594	.7546	.7499	.7452
12	.7406	.7360	.7314	.7268	.7223	.7178	.7133	.7089	.7044	.7000	.6957	.6913
15	.6870	.6827	.6785	.6742	.6701	.6659	.6617	.6576	.6535	.6494	.6454	.6413
18	.6373	.6334	.6294	.6255	.6216	.6177	.6139	.6100	.6062	.6024	.5987	.5949
21	.5912	.5875	.5839	.5802	.5766	.5730	.5695	.5659	.5624	.5589	.5554	.5519
24	.5485	.5451	.5417	.5383	.5349	.5316	.5283	.5250	.5217	.5184	.5152	.5120
27	.5088	.5056	.5025	.4993	.4962	.4931	.4901	.4870	.4840	.4809	.4780	.4750
30	.4720	.4691	.4661	.4632	.4603	.4575	.4546	.4518	.4489	.4462	.4434	.4406
33	.4379	.4351	.4324	.4297	.4270	.4244	.4217	.4191	.4165	.4139	.4113	.4088
36	.4062	.4037	.4011	.3986	.3961	.3937	.3912	.3888	.3864	.3840	.3816	.3792
39	.3768	.3745	.3721	.3698	.3675	.3652	.3629	.3607	.3584	.3562	.3540	.3518
42	.3496	.3474	.3452	.3431	.3409	.3388	.3367	.3346	.3325	.3304	.3284	.3263
45	.3243	.3223	.3202	.3183	.3163	.3143	.3123	.3104	.3084	.3065	.3046	.3027
48	.3008	.2989	.2971	.2952	.2934	.2916	.2897	.2879	.2861	.2844	.2826	.2808
51	.2791	.2773	.2756	.2739	.2722	.2705	.2688	.2671	.2654	.2638	.2621	.2605
54	.2589	.2573	.2557	.2541	.2525	.2509	.2493	.2478	.2462	.2447	.2432	.2417
57	.2402	.2387	.2372	.2357	.2342	.2328	.2313	.2299	.2284	.2270	.2256	.2242
60	.2228	.2214	.2200	.2186	.2173	.2159	.2146	.2132	.2119	.2106	.2093	.2080
63	.2067	.2054	.2041	.2028	.2016	.2003	.1991	.1978	.1966	.1954	.1941	.1929
66	.1917											

APPENDIX C. DECAY FACTORS FOR PLUTONIUM-236

The following table gives the fraction of activity remaining after the time interval between the standardization count and the sample count. If the time interval exceeds 31 days, multiply the factors. For example, the factor for 31 + 30 + 9 = 70 days is 0.9796 × 0.9802 × 0.9940 = 0.9544.

Days	A/A_0
0	1.0000
1	.9993
2	.9987
3	.9980
4	.9973
5	.9967
6	.9960
7	.9953
8	.9947
9	.9940
10	.9934
11	.9927
12	.9920
13	.9914
14	.9907
15	.9901
16	.9894
17	.9887
18	.9881
19	.9874
20	.9868
21	.9861
22	.9854
23	.9848
24	.9841
25	.9835
26	.9828
27	.9822
28	.9815
29	.9809
30	.9802
31	.9796

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ERRATA

"Handbook of Radiochemical Analytical Methods," EPA-680/4-75-001, February 1975, National Environmental Research Center, U.S. Environmental Protection Agency, Las Vegas, Nevada.

Page 4.	Steps 9 and 10 are given in reverse order. Substitute the enclosed page 4 for the one in error.
Page 63.	Change Tiritum to Tritium in list of Reagents.
Page 72.	Figure 10. Change "Iron Cathode" to "Iron Anode."
Page 129.	Equation at bottom of page for lead-210 activity at time of original separation should read:

$$\text{Lead-210 at } t_1 \pm 2\sigma \text{ at } t_1 = \frac{\lambda_{\text{Po-210}}}{\lambda_{\text{Pb-210}}} \times \frac{\text{Pb-210 at } t_2 \pm 2\sigma \text{ at } t_2}{1 - e^{-\lambda(t_2 - t_1)}}$$

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5. Collect the first 400 ml of eluent in a 500-ml centrifuge bottle at a flow of 20 ml/min. See Note a to regenerate the resin.

6. Add 1 ml 6N sodium hydroxide to the 400-ml strontium-barium fraction, and with stirring add 10 ml 3N sodium carbonate. Continue stirring for 30 minutes (Note b). Centrifuge, and discard supernate.

7. Dissolve the precipitate with 5 ml 1N nitric acid and transfer to a 40-ml centrifuge tube. Add 5 ml ammonium acetate buffer (pH 5.25) to the centrifuge tube, rinse by rolling, and again transfer to a 40-ml centrifuge tube. Adjust pH to 4.6 with concentrated ammonium hydroxide and/or 1N nitric acid. Heat in water for 5 minutes and add 1 ml 1N sodium chromate. Stir for 10 minutes to precipitate barium. Centrifuge, and discard precipitate. Repeat.

8. Add 2 ml concentrated ammonium hydroxide to the supernate and swirl tube to mix well. Add 2 ml 3N sodium carbonate to reprecipitate the strontium. Centrifuge, and discard the supernate.

9. Wash precipitate with distilled water, centrifuge, and discard supernate. Repeat.

10. Dissolve the precipitate in a maximum of 6 ml 3N nitric acid. Add 30 ml fuming nitric acid to the solution to precipitate strontium nitrate. Cool the solution in an ice bath, centrifuge, and discard the supernate. Record time and data as T_1 (start of yttrium ingrowth).

11. Transfer the precipitate to a clean, tared planchet with a minimum of distilled water. Dry, cool, and weigh. Count on a low-background beta counter.

12. Count again seven days later for yttrium-90 ingrowth and strontium-89 decay.

Notes: a. To prepare the resin in the Na^+ form, wash 170 ml of resin (H^+ form) with 1000 ml of 4N sodium chloride eluted at 10 ml/min, followed by 400 ml of 5% sodium hydroxide at 10 ml/min, then 1000 ml of distilled water at 10 ml/min flow rate. Repack column and add glass fiber filter to top of column.

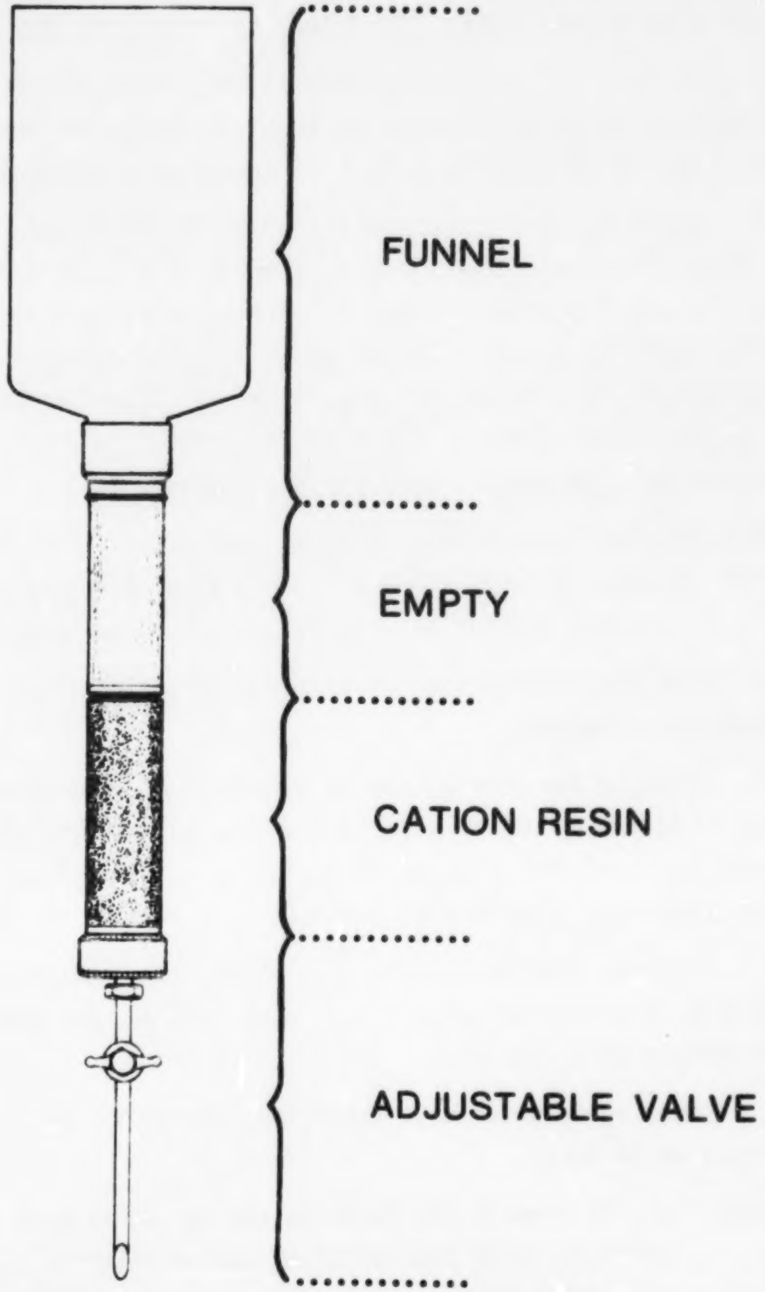
FUNNEL
EMPTY
CATION RESIN
ADJUSTABLE VALVE

Figure 1. Ion Exchange Column